Contaminants of Emerging Concern in Mediterranean Watersheds

Maja Kuzmanovic, Antoni Ginebreda, Mira Petrovic, and Damià Barceló

Abstract The present chapter provides a general perspective on the occurrence, ecotoxicological risk, and prioritization of emerging and classical contaminants in Mediterranean river basins with special focus on the Iberian Peninsula as representative case, in the light of the results recently obtained. Risk assessment and prioritization criteria based on ecotoxicological risk with respect to different trophic levels are explained and applied to the Mediterranean basins studied. This enables to rank contaminants according to their ecotoxic risk and to quantify their joint effect as a mixture on a river site.

Keywords Compound prioritization, Emerging contaminants, Mediterranean rivers, Priority contaminants, Risk assessment, Risk index, Toxic units

Contents

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1 Introduction

Chemical pollution of aquatic ecosystems is one of the major threats to aquatic life biodiversity and human health [1]. Increasing pollution of water with a variety of chemical compounds, with their mostly unknown long-term effects, could easily lead to environmental problems of great magnitude [2]. In the coming century, climate change and a growing imbalance among freshwater supply, consumption, and population will alter the water cycle dramatically [3]. In the European Union, there are more than 100,000 registered chemicals listed by EINECS (the European Inventory of Existing Commercial Chemical Substances), of which many are in everyday use. There are many possible sources of pollutants in the environment such as surface runoff from agricultural and urban areas, through industrial and urban wastewater discharge, atmospheric deposition, accidental spills, etc. Some compounds are not properly eliminated by wastewater treatments and are continuously released into the environment as a part of the effluent. Most of these chemical compounds are present in the environment at low concentrations, but still many of them may possibly be a threat to different biological end points [2]. Given the huge number of chemicals present in the environment and their potential adverse effects, there is a need to prioritize chemicals according to the risk they pose to the ecosystem. Prioritization of chemicals is necessary for optimization monitoring efforts, to provide appropriate and scientifically sound information to legislators and water managers. To provide this information, many environmental risk assessment approaches have been developed [4].

In the European Union, the legislation considering aquatic environment protection is mostly covered by the introduction of the Water Framework Directive (WFD) in year 2000. The aims of WFD are to achieve good ecological and good chemical status of European surface waters. The WFD issued the list of priority and hazardous substances including contaminants which are recognized for their adverse effects, mainly on the basis of persistence, bioaccumulation, and toxicity properties (PBT). In order to achieve good chemical status, the Environmental Quality Standards (EQS) of the priority pollutants must be met [5], that is, the levels of concentrations of these compounds must be below the EQS. Moreover, recently the European Commission issued a proposal for updating the list of priority substances by adding 15 new candidates. Member states are obliged to identify river basin-specific pollutants, i.e., the pollutants of regional and local importance. Moreover, regulated chemicals that are monitored on a regular basis are just a small fraction of numerous chemicals present in the environment [6]. Many emerging contaminants are detected due to improvement of analytical techniques [7, 8]. They might be ecotoxicologically relevant compounds as well, especially when present as the constituents of the complex chemical mixtures in the environment [2]. Therefore, it is necessary to evaluate the risk of emerging contaminants and if necessary to include them into the monitoring and regulation programs [9]). Representative examples of compounds that are considered as emerging contaminants or contaminants of emerging concern are pharmaceuticals and personal care products, polar pesticides, natural toxins, biocides, perfluorinated compounds, and nanomaterials, among others.

One approach for identifying potentially dangerous compounds is screening of the environment for a large set of chemicals together with an assessment of the potential toxicity at the observed concentrations [10].

Generally, the ecotoxicity of a given pollutant is determined by standardized tests, with the use of selected model organisms and toxicity end points, such as acute toxicity or lethality in algae, invertebrates, and fish so that different trophic levels are covered as recommended by WFD [11].

2 Pollution of Mediterranean Rivers

In the SCARCE Consolider project [12], four Iberian river basins were studied as the representatives of Mediterranean region river basins. The samples of water, sediment, and biota were collected at 77 sampling sites for chemical characterization (Fig. 1). Studied river basins are situated in areas of multiple land use types, from natural forests and grasslands to agricultural lands and highly industrialized and urbanized areas. The pollution of rivers is reflecting the land use in the chemical mixtures present in water. Each of the river basins has a different proportion of land use types and the number and concentrations of chemicals detected (Table 1). In general, more than 50 chemicals were detected in each sample. Of the studied groups of chemicals, industrial organic compounds were measured at highest concentrations in majority of samples except in Júcar where pesticides as a group were measured at highest concentrations (Fig. 6). A high number of pharmaceuticals were detected in all four rivers, as well as several hormones, personal care products, and illicit drugs related to urban zones.

In brief, Llobregat was the most contaminated river in terms of number and concentration of organic compounds detected. Several sampling sites in Ebro were highly polluted by a variety of chemicals. Júcar pollution was mainly dominated by pesticides. Guadalquivir was the least contaminated of studied river basins.

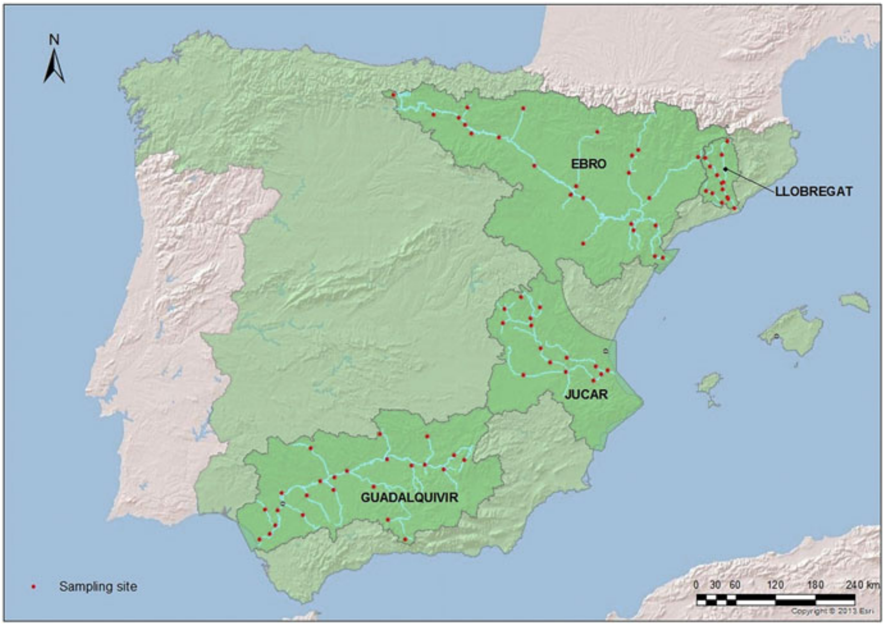

Fig. 1 SCARCE project sampling sites

Table 1 Minimum and maximum number of individual chemicals of each compound group detected in samples analyzed

Number of chemicals detected in sample	Llobregat	Ebro	Júcar	Guadalquivir	Reference
Pesticides	6–11	6–17	6–17	8–15	[13]
IOCs	6–9	5–10	5–9	7–12	[14]
PFCs	0–10	0–8	1–9	3–9	[13]
Pharmaceuticals	10–55	9–60	35–40	9–35	[15]
PCPs	0–10	0–7	3–7	2–8	[14, 16]
Hormones	1–3	0–5	0–3	0–4	[14]
Illicit drugs	0–4	0–4	0–4	0–3	[17]

IOCs industrial organic chemicals, *PFCs* perfluorinated compounds, *PCPs* personal care products

2.1 Llobregat

The Llobregat river basin is located northeast of Spain. The lower part of the basin is highly urbanized and densely populated, so the anthropogenic pressure at that area is the strongest [18] (Fig. 2). Surface runoff and industrial and urban wastewaters discharges are possible sources for pollutants in river water and sediment. Agricultural lands are surrounding the urban zones, so diffuse pollution from agriculture is also present. In spite of the severe pressures it receives, Llobregat is

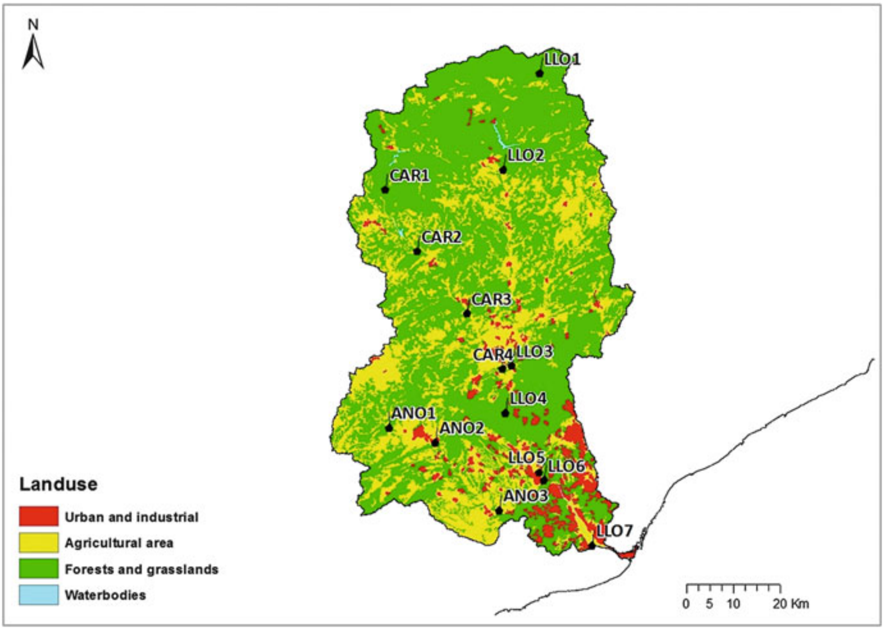

Fig. 2 Land use types in Llobregat river basin and sampling sites of SCARCE project

the drinking water supply for Barcelona and surrounding cities. Due to the Mediterranean climate characteristic for this geographical area, this river is subjected to periodic drought periods which lead to water scarcity and therefore to reduced dilution capacity of the river. In these periods, the risk to the aquatic ecosystem could be increased because of the higher exposure of biological communities to pollutants.

There is a notable increase of pollution downstream (Fig. 3), particularly in the lower part of the basin, close to the mouth of the river (LLO5, LLO6, and LLO7), and in the Anoia tributary (Sites ANO1, ANO2, and ANO3) which is passing through the industrial area of Igualada not far away from Barcelona city. The compound group measured at highest concentration at the majority of sampling sites was industrial organic compounds (IOCs, gray color). Of the compounds belonging to this group, alkylphenols (octylphenol, nonylphenol, and related compounds) and anticorrosion agents as tolyltriazole and 1H-benzotriazoles were the most relevant. The highest concentration of IOCs was measured at site LLOB7 (Fig. 3), the most downstream site in the basin (IOCs = 10.5 μg/L). Pharmaceuticals are the second group in terms of concentration, especially in the lower, urbanized part. Perfluorinated compounds (PFCs) were measured in Anoia tributary with concentration up to 2.8 μg/L which was measured at site ANO2. The most abundant compounds of this group were perfluorobutanoic acid (PFBA) and perfluorooctanesulfonic acid (PFOS), the latter included in the WFD priority list.

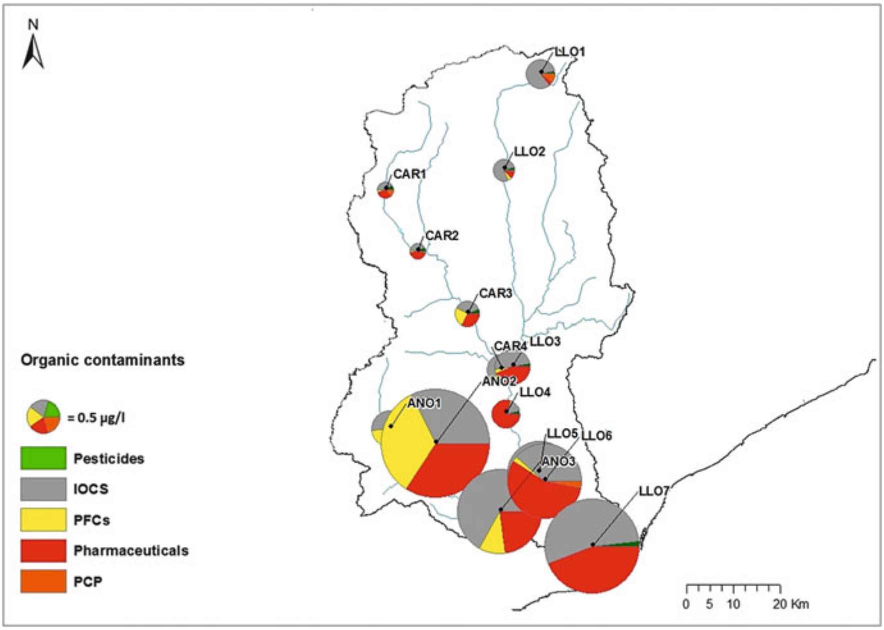

Fig. 3 Pollution of Llobregat river water with organic chemicals

2.2 Ebro

The Ebro river basin is located northeast of the Iberian Peninsula. It generates the delta and the big wetland area (320 km) with a specific biodiversity and a high ecologic value. A large share of land in this basin is devoted to agriculture (Fig. 4). Along the river, there are the fields for cereal and corn cultivation, vineyards, fruit orchards, etc. and for the delta rice production and horticulture. Precipitation decrease, increase of water demand for irrigation in agriculture, reforestation, and several other factors caused the river flow decrease of approximately 40% in the last century. The population is concentrated in several big cities like Pamplona, Zaragoza, and Lleida, mainly, in the northern and central part of the basin. Industrialized areas are surrounding the cities, so the urban types of pressures to water quality are located in several spots, while agricultural pollution potential is present along the basin.

In Ebro, the highest organic contaminant concentration was measured at Zadorra site (Fig. 5; ZAD, approx. 10 μg/L) sampled close to wastewater treatment plant, downstream of Basque city Vitoria. Industrial organic chemicals were the major group of contaminants at almost all sampling sites. The second group corresponded to pharmaceuticals, which included the compounds belonging to different therapeutic classes. The maximum concentration of pharmaceuticals was measured at the aforementioned Zadorra site (Fig. 5). The concentration levels of pesticides are relatively higher at sites in the lower part of the basin and Ebro delta. At sites

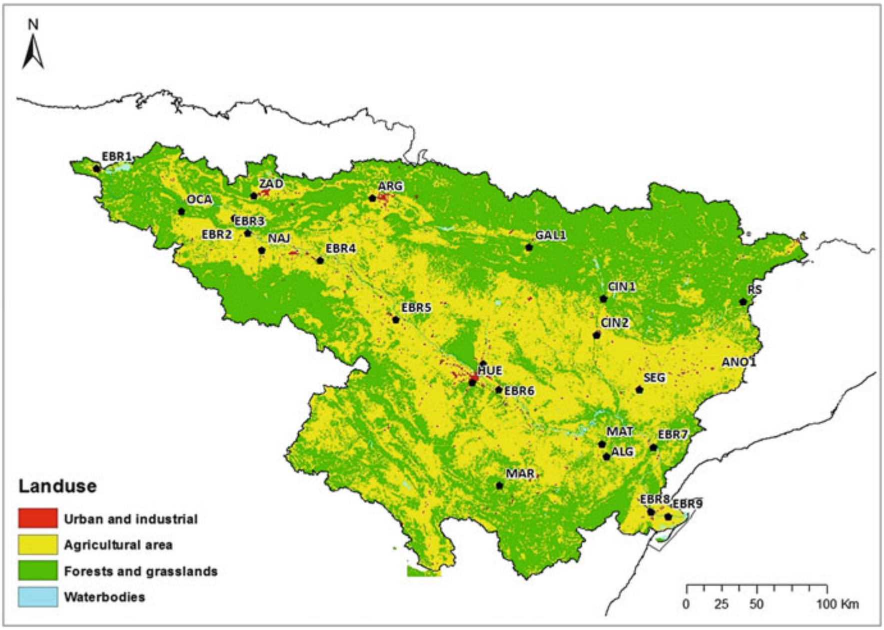

Fig. 4 Land use types in Ebro river basin and sampling sites of SCARCE project

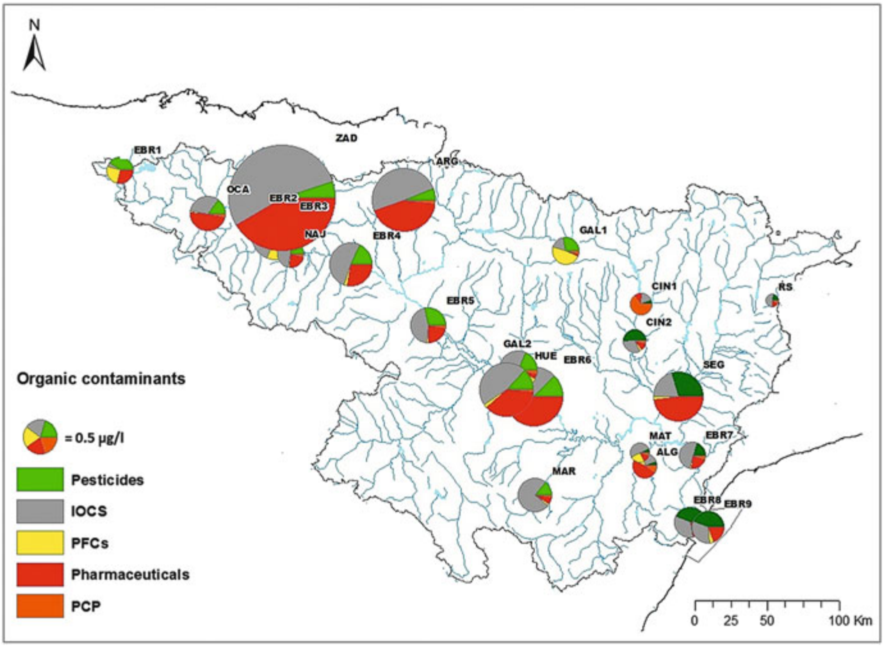

Fig. 5 Pollution of Ebro basin

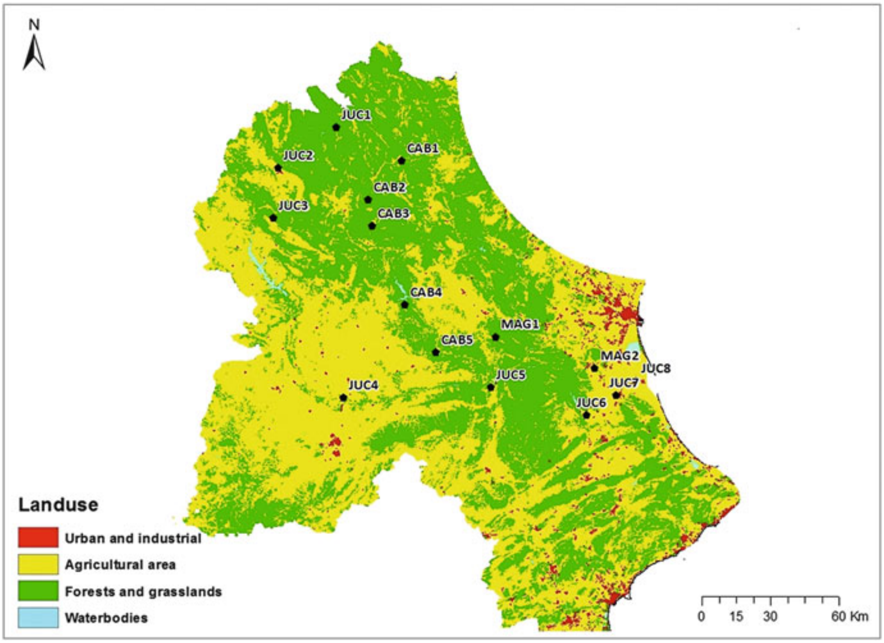

Fig. 6 Land use types in the Júcar river basin and sampling sites of SCARCE project

situated in the delta where agriculture is very developed (Ebro 8 and Ebro 9), pesticides are the major pollutant group measured. Compared to heavily contaminated sites like Zadorra or Arga, the total concentration of organic contaminants is relatively small (approx. 0.5 μg/L).

2.3 Júcar

The Júcar river basin is located east of Spain. It has a population of approximately 2.5 million inhabitants mainly located in the coastal area of the basin. Agricultural lands used for rice production, citrus fruit growth, etc. are located in the lower part of the basin surrounding the urban and industrial zones and in the southeast at the less urbanized zone (Fig. 6). The basin is situated in an area of semiarid climate which is adding to the problem of overexploitation of water for agricultural purposes and other uses resulting in decreasing the flow. The lower part of the basin is impacted by urban, industrial, and agricultural pressures influencing on the water quality.

Pesticides were the main group of pollutants found at majority of the sites of the Júcar basin (Fig. 7). Industrial organic compounds were measured at highest concentration at MAG1 site which is also the most polluted site in the river basin with the concentration of organic contaminants approximately 4 μ/L.

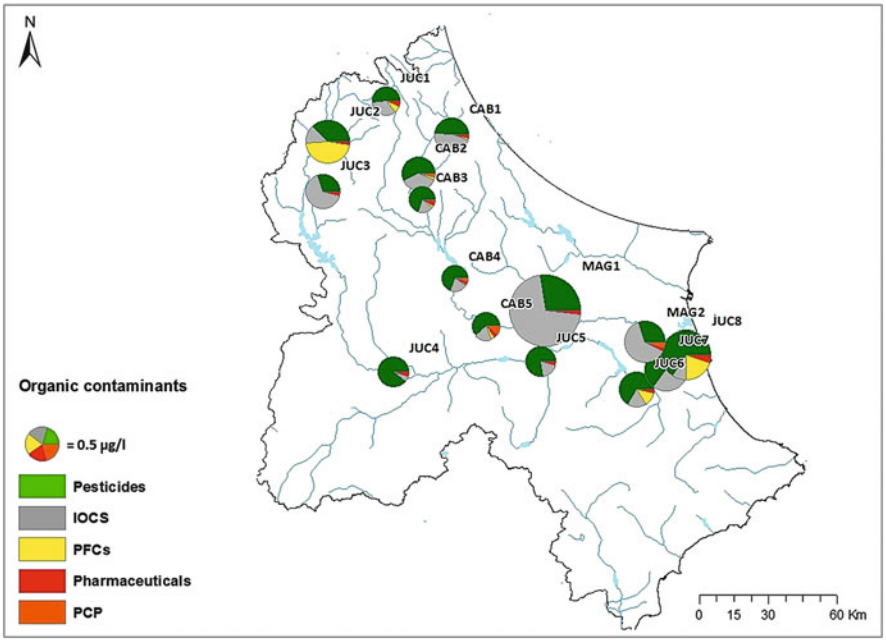

Fig. 7 Pollution of river Júcar with organic pollutants

Comparatively, pharmaceuticals and personal care products were measured at lower concentrations than in Ebro and Llobregat.

2.4 Guadalquivir

The Guadalquivir river basin is situated southwest of the Iberian Peninsula. The large proportion of the land is used for agricultural purposes (Fig. 8) with cultures such as olive trees, grapes, sugarcane, corn, etc. Mediterranean fruits and rice are grown in the lowest part of the basin. The delta is an area of high ecological value constituting the Doñana National Park. The Guadalquivir river together with its tributaries represents the main water source of the region serving the population of big cities such as Granada, Córdoba, and Seville. As a consequence of the high population of the cities, the river receives many inputs from the anthropogenic sources that may cause deterioration of water quality, together with the runoff of pesticides and fertilizers from agricultural areas.

Compared to other studied basins, Guadalquivir was the least contaminated. The main pollutants group in Guadalquivir was, like in Ebro and Llobregat, industrial organic compounds. The following group in terms of concentrations was perfluorinated compounds. The pollution was slightly higher in lower and middle part of the basin (Fig. 9).

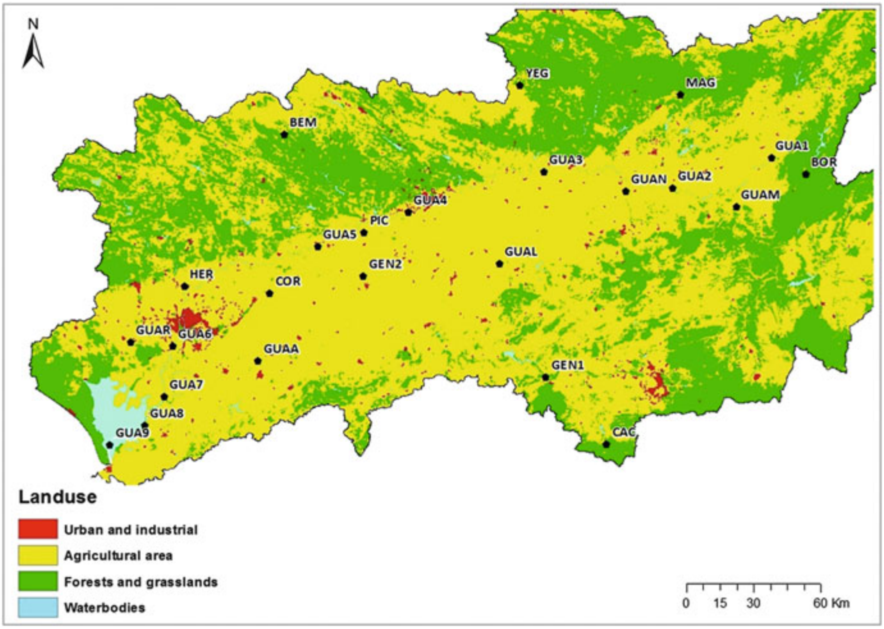

Fig. 8 Land use types of Guadalquivir basin

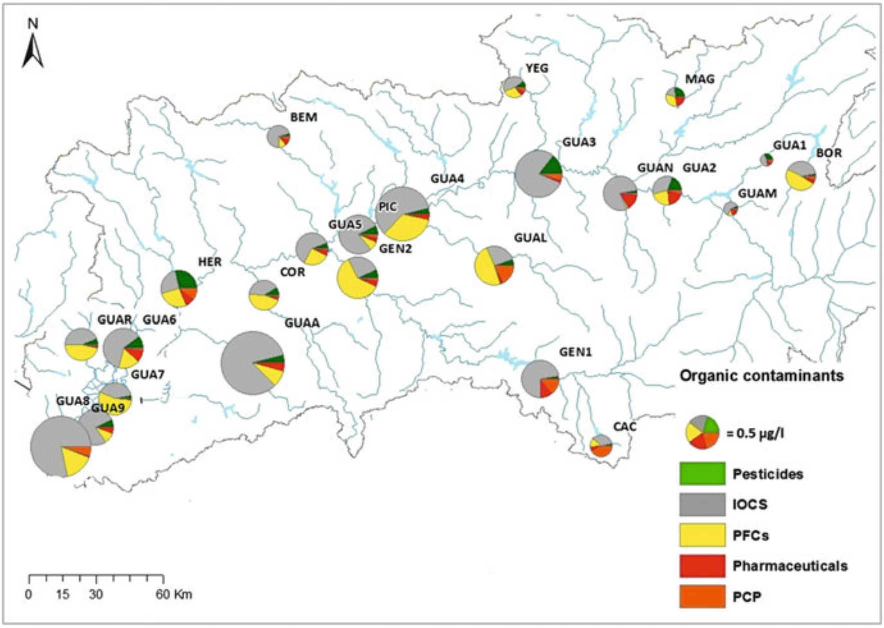

Fig. 9 Organic pollution of Guadalquivir river basin

3 Risk Assessment of Chemical Pollution in Iberian Basins

In order to assess the risk of chemical pollution [19, 20] and to determine the compounds of highest priority in four Iberian river basins [19, 20], the so-called toxic unit (TU) approach [21] was used to determine the ecotoxicological risk of individual compounds detected. Both aspects are developed in the following sections.

3.1 Toxic Units

Toxic unit is defined as the ratio of measured or predicted concentration of the compound and the corresponding toxicity value. In the aforementioned studies, measured concentration of compounds was used (C_i) together with acute toxicity data for three standard test species algae *Pseudokirchneriella subcapitata*, invertebrate *Daphnia magna*, and fish *Pimephales promelas*, representatives of trophic. EC50 values for algae and invertebrates (effect concentration for 50% of individuals at 48 or 96 h exposition time) and LC50 values for fish (lethal concentration for 50% of individuals) were used (Eq. 1). Toxicity data measured in vivo were collected from databases such as ECOTOX [37], Pesticides Properties DataBase [36], PAN Pesticide Database [22], and ECHA [23] or were collected from the literature. Missing data were evaluated by ECOSAR.

$$\mathrm{TU}_{i\ (\text{algae, invertebrates and fish})} = \log \frac{C_i}{\mathrm{EC50}_i} \tag{1}$$

where TU_i is the toxic unit of the compound i, C_i (μg/L) is the measured concentration in the water phase, and EC50 is the effect concentration for the same compound (EC50 for algae and invertebrates and LC50 (μg/L) for fish, respectively). For convenience we express TUi in log units along the present chapter.

For the sediment toxic unit calculation, bioavailable pore water concentration was estimated following equilibrium partitioning approach [24]. From the bulk sediment concentrations measured, the bioavailable fraction of contaminants in the pore water was predicted by using the partitioning coefficient between sediment and water (K_d) (Eq. 2) as suggested by several authors [25].

$$C_\mathrm{S} = C_\mathrm{PW} \times K_\mathrm{d} \tag{2}$$

K_d is the partitioning coefficient between water and sediment, C_S the bulk sediment concentration, and C_PW the pore water concentration of the contaminant.

Therefore, sediment toxic units were defined as the ratio of the estimated pore water concentration of a contaminant and the water exposure-based toxicity values. Since the organic matter is assumed to be the major binding phase for nonionic organic chemicals in sediments [24], fraction of organic carbon in sediment (f_{oc}) and partitioning coefficient between organic carbon and water (K_{oc}) were used to calculate the pore water concentration (Eq. 3):

$$C_{PW} = \frac{C_S}{f_{OC} \times K_{OC}} \quad (3)$$

3.2 Site-Specific Risk

To assess the risk of chemical pollution at each sampling site, site-specific toxic unit (TU_{Site}, Eq. 4) was calculated as the sum of TUs of the compounds detected at that site [19, 20]. The concentration addition (CA) concept [26] mixture toxicity model was followed. It is generally used as the first tier approach, especially in the cases when the modes of action of many compounds in the sample are not known. The site-specific risk was expressed as the logarithm of the sum of individual toxic units (Eq. 2):

$$TU_{SITE} = \log \sum_{i=1}^{n} TU_i \quad (4)$$

where TU_i is the toxic unit of each of individual compounds at the site.

Furthermore, the thresholds for effects in ecosystems were set as proposed in the study by Malaj et al. [27]. Acute risk threshold of $TU \geq -1$, corresponding to 1/10 of the EC50 or LC50 of all three standard test species, was chosen due to the fact that changes in biological communities exposed to this level of pollution were observed [28–30]. On the other hand, different chronic risk thresholds were used for algae, invertebrates, and fish. Value of $TU \geq -3$ was used for invertebrates based on the field studies; chronic risk thresholds for algae and fish were based on acute to chronic ratio [27]. For algae the acute to chronic factor 5 was used and for fish factor 10 [31–33].

3.3 Acute and Chronic Effect Risk in Iberian Rivers

Based on this risk assessment approach, there was risk of acute effects at 42% of the sampling sites and risk of chronic effects at all sampling sites in river basins studied. Risk was higher in 2010, when there was acute risk threshold exceedance at 42% of sites for invertebrates and 3% for fish. In 2011 there was exceedance at 20% of the sites for invertebrates and no exceedance for algae and fish. Even though Llobregat was the most polluted of this four rivers, the risk was the highest in Ebro (74% of the sites with acute risk) and Júcar (67% of the sites with acute risk), while in Llobregat, there was less than 25% of the sites with acute risk (Fig. 10). The river and campaign showing the highest number of sites with acute risk was the Ebro in

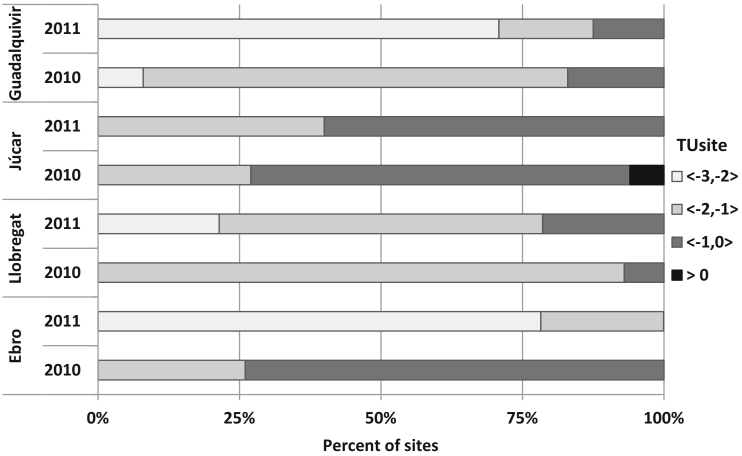

Fig. 10 Percentage of sampling sites with TU_{site} (most sensitive test species) belonging to one of four toxic unit ranges for each of four river basins in 2010 and 2011 in four studied basins. Dark gray shades, toxic units associated with acute effects; light gray shades, toxic units associated with chronic effects

2010 due to high concentration of toxic pesticides. However, they were not present at such high concentrations in 2011, so the acute risk threshold was not exceeded even though many other compounds were detected, indicating the importance of pollutant prioritization for monitoring and regulation purposes. In Guadalquivir, there was the smallest number of sites with acute risk exceedance (Fig. 10). In general, of studied organic chemicals, only pesticides present in water were related to acute risk. However, other groups of compounds (pharmaceuticals, personal care products, industrial organic compounds, etc.) were related to chronic risk threshold exceedance.

4 Prioritization of Pollutants in Iberian Basins

Of all the compounds present in the environment, typically there are only few which are responsible for the majority of the risk for biological communities [26]. Therefore, for the risk mitigation purposes, it is crucial to identify those compounds that are the most important in terms of ecotoxicological risk for each of studied river basins. To cope with this, ranking index [19, 20] was developed to prioritize the compounds on the basis of their ecotoxicological potential and distribution of concentrations along the river basin. The approach is based on toxic unit concept (TU) [21].

Table 2 Ranks of toxic units with corresponding weights

Rank (X)	Range (TU)	Weight (w_x)
1	>0	1
2	<0, −1>	0.5
3	<−1, −2>	0.25
4	<−2, −3>	0.125
5	<−3, −4>	0.0625
6	<−4	0

4.1 Ranking Index

Ranking index (RI) for prioritization was developed based on the previously used prioritization approach by von der Ohe et al. [10]. For calculating the ranking index, toxic units were ranked into six ranges, and to each of them a different weigh is assigned (Table 2).

The ranks are covering the ranges of toxic unit that could be related with acute and chronic effects in ecosystems, and for the lowest rank, TU level of −4 is taken, for which no effects are expected in most of the cases [34, 35]. Rank frequencies f_x are calculated as a percentage of the sites in the river basin where TU of the compound belongs to one rank (Eq. 4):

$$f_x = \frac{n_x}{N_{\text{total}}} \ (\%) \tag{4}$$

where n_x is the number of sites in the river basin with toxic unit level falling in rank x and N_{total} is the total number of sampling sites in river basin. The sum of all rank frequencies is equal to 100% as it covers all the sampling sites. The ranking index of the compound in the studied basin is calculated by the sum of the rank frequencies f_x multiplied by the given rank weights w_x (Eq. 5):

$$\begin{aligned}\text{Ranking index} = \sum_{x=1}^{6} f_x \cdot w_x = \ & (f_1 \times 1) + (f_2 \times 0.5) \\ & + (f_3 \times 0.25) + (f_4 \times 0.125) + (f_5 \times 0.0625) + (f_6 \times 0.0)\end{aligned} \tag{5}$$

The ranking index is scaled from 0 to 100, where 0 signifies that the toxic units of the compound were below the risk threshold of −4 at all the sampling sites. On the contrary, RI of 100 means that the toxic units of the compound were above 0 at all sampling sites. That is, the threshold for acute effect risk, EC50 or LC50 (for algae and invertebrates and fish, respectively), of standard test species concerned is exceeded at all sites.

4.2 Prioritization of Water and Sediment Pollutants

Ranking indexes were calculated related to toxic units of algae, invertebrates, and fish separately to cover the risk of compounds to different trophic levels. The ranking index values then can be used to give the information of the risk of the compound in the studied river basin. In particular, the values of RI give us the idea whether the compound is in high or low toxic units or below toxicity threshold (RI = 0%) in the studied river basin. We considered the RI higher than 12.5%, as the value of classifying the compound as the most important for studied area. This value means the compound was both in high toxic units and frequently exceeded the toxicity threshold of −4. The compounds which were classified as the most important for each of the studied river basins are represented in Table 3 and other compounds that were either in low toxic units at many sampling sites or at high toxic units but only at the few sampling sites in Table 4.

The most important compounds for studied river basins were mainly pesticides and industrial organic compounds. Among them, two pesticides classified as priority pollutants of WFD were ranked the highest. Pesticides as chlorpyrifos and chlorfenvinphos are the highly toxic compounds, designed to be biologically active even at low concentrations. However, when present in the environment, they might cause acute effects on nontarget species. Therefore, if they are frequently found in high toxic units in river basin, we might expect losses of biodiversity in local biological communities.

Compounds for which RI was between 0 and 12.5% are listed in Table 3. Several pharmaceuticals like sertraline, losartan, etc. were found at low TU at many sites in the studied rivers (Table 4). Therefore, their chronic effects could not be excluded. But, for more accurate risk assessment of chronic effects, chronic toxicity data should be used. However, chronic toxicity data for pharmaceuticals and other emerging contaminants is in fact very scarce. Several pesticides were in high TU

Table 3 Most important water pollutants in studied basins according to RI based on toxicity to algae, invertebrates, and fish

	Llobregat			Ebro			Júcar			Guadalquivir		
Compound	**A**	**D**	**F**	**A**	**D**	**F**	**A**	**D**	**F**	**A**	**D**	**F**
<u>Chlorpyrifos</u>		**X**	**X**		**X**			**X**	**X**		**X**	
<u>Chlorfenvinphos</u>					**X**			**X**			**X**	
Dichlofenthion					**X**	**X**		**X**	**X**			
Diazinon		**X**			**X**			**X**			**X**	
Prochloraz							**X**					
Ethion								**X**				
Carbofuran		**X**										
<u>OPs/NPs</u>		**X**									**X**	
Diuron	**X**											

Underlined WFD priority pollutants
A algae, *D Daphnia magna*, *F* fish

Table 4 Other important pollutants for each of the studied basins according to RI in water

	Llobregat			Ebro			Júcar			Guadalquivir		
Compound	A	D	F	A	D	F	A	D	F	A	D	F
Sertraline	**X**	**X**		**X**			**X**					
Triclosan	**X**			**X**			**X**			**X**		
Parathion-ethyl					**X**			**X**				
Caffeine	**X**			**X**			**X**			**X**		
Terbutrine	**X**			**X**								
Isoproturon	**X**			**X**								
Losartan	**X**			**X**	**X**							
Imazalil				**X**		**X**	**X**	**X**	**X**			
Tolyltriazole	**X**	**X**		**X**						**X**		
Simazine	**X**			**X**						**X**		
Atrazine				**X**			**X**			**X**		
Azinphos-ethyl		**X**			**X**						**X**	
Malathion		**X**	**X**		**X**			**X**	**X**		**X**	**X**
Azinphos-methyl		**X**			**X**							
Thiabendazole					**X**							
Methiocarb		**X**			**X**						**X**	
Venlafaxine	**X**	**X**		**X**	**X**							
Gemfibrozil			**X**									**X**
Pyriproxyfen						**X**			**X**			

Underlined WFD priority pollutants
A algae, *D Daphnia magna*, *F* fish

Table 5 Most important sediment pollutants for each of the studied basins according to RI

	Llobregat			Ebro			Júcar			Guadalquivir		
Compound	A	D	F	A	D	F	A	D	F	A	D	F
Chlorpyrifos		**X**	**X**		**X**	**X**		**X**	**X**		**X**	**X**
Chlorfenvinphos											**X**	
Nonylphenol	**X**	**X**	**X**								**X**	**X**
Diazinon		**X**						**X**			**X**	
Malathion								**X**				
Ciprofloxacin										**X**	**X**	
Methiocarb								**X**				

Underlined WTD priority pollutants
A algae, *D Daphnia magna*, *F* fish

but only at few sites in the studied basins; therefore, their ranking index was relatively low. That is, they may pose high risk, but only at specific areas of the basins concerned.

As regards to sediments, pesticides as chlorpyrifos and chlorfenvinphos were the most important pollutants according to the ranking index (Table 5). They were in higher concentrations in sediment; therefore, the ranking index was higher as well (chlorpyrifos max $RI_{sediment} = 80\%$; max $RI_{water} = 35\%$).

5 Conclusions

The four Mediterranean Iberian river basins studied were found contaminated by a variety of man-made compounds. In general, there were more than 50 compounds detected in each sample, including pesticides, pharmaceuticals, different industrial compounds, personal care products, and other types of contaminants. Llobregat was the most polluted of studied rivers, especially the lower part of the river which is passing through highly industrialized and urban zones. However, the ecotoxicological risk was the highest in Ebro and Júcar due to presence of acutely toxic pesticides in water. There was risk of acute effects posed by organic compounds at altogether 42% of the sampling sites and risk of chronic effects at all the sites. Pesticides were the compounds responsible for acute risk at the four rivers. However, other compounds like industrial organic compounds and emerging contaminants like pharmaceuticals and personal care products were responsible for the chronic risk threshold exceedance as well. A ranking index (RI) was used to order the compounds according to their environmental risk which takes into account both the frequency of occurrence and the ecotoxicological relevance (levels of toxic units) . In the studied river basins, nine compounds were regarded as the most important water pollutants (chlorpyrifos, chlorfenvinphos dichlofenthion, etc.) and seven compounds as the most important sediment pollutants (chlorpyrifos, chlorfenvinphos, nonylphenol, etc.).

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