CONTRIBUTIONS to SCIENCE
OPEN ACCESS

CONTRIB SCI 10:125-134 (2014)
doi:10.2436/20.7010.01.197

ARTICLE

Institut d'Estudis Catalans, Barcelona, Catalonia
www.cat-science.cat

Risk assessment and prioritization of pollutants in continental Mediterranean waters based on hazard quotients

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Summary. The input of chemical pollutants into the aquatic environment is growing but their potential adverse effects on the ecosystem still remain largely unknown. Therefore the development of appropriate risk assessment procedures capable to provide a prioritization of potential pollutants becomes necessary. Here we identify priority compounds specific to Mediterranean rivers and compare them to those found in other rivers worldwide. To this purpose *hazard quotients* (HQ) defined as the ratio of *measured environmental concentration* (MEC) to *predicted non effect concentration* (PNEC) referred to different trophic levels were calculated for different compounds selected from different existing prioritization schemes, as well as 15 priority substances identified under the Water Framework Directive (WFD) and compared for cases of Mediterranean vs. North European and USA rivers. [**Contrib Sci** 10:125-134 (2014)]

Introduction

Pollution is recognized nowadays as one of the major threats to aquatic systems [28]. Although most of these chemical compounds are present at low concentrations, many of them may raise serious toxicological concerns [26]. In the European Union (EU) there are more than 100,000 registered chemicals listed by EINECS (The European Inventory of Existing Commercial Chemical Substances) of which 30,000 to 70,000 may be considered of common industrial and/or domestic use. Depending on their physico-chemical properties, amounts produced and mode of use many of these compounds may enter the natural waters through sewage water discharge, surface runoff from agricultural fields, atmosphere deposition, accidental spills, etc. On the other hand, many of these compounds are not properly eliminated by conventional wastewater treatment plants and are being continuously released as a part of the effluent. Given the huge number of chemicals potentially released into the environment and existing time and budget constrains there is a need to prioritize chemicals in order to optimize monitoring efforts, as well as to provide appropriate and scientifically sound

Keywords: pollutants · risk assessment · ecotoxicity · hazard index · prioritization of pollutants

information to both legislators and water managers. This is the purpose aimed by the environmental risk assessment process [27].

Considering current legislation, in the European Union, the big upturn in aquatic environment protection was made by the introduction of the Water Framework Directive (WFD) that was established in 2000 and aimed to achieve good ecological and good chemical status of European surface waters by the year of 2015. Using combined monitoring- and modeling-based priority setting scheme, WFD identifies a list of 33 priority substances that pose a significant risk to the EU aquatic environment [11] and 8 other hazardous substances from previous legislation. The lists of priority and hazardous substances include contaminants that have been long recognized as dangerous, especially for the human health and are regulated mainly on the basis of persistence, bioaccumulation and toxicity properties (PBT). In order to achieve good chemical status, water bodies of the EU member states must meet the *environmental quality standards* (EQS) [10] (i.e., to keep the levels of concentrations of these compounds below the EQS). Furthermore, it is expected to update and review the list of priority substances every 4 years. In this context, recently the European Commission has updated the list of priority substances by adding 15 new candidates. EU member states are obliged to identify pollutants of regional or local importance and provide EQS, monitoring schemes and regulatory measures for them. This means that member states need to decide which are the candidate substances for further investigation and which are the substances to be then declared as river basin specific pollutants [23]. Due to specific bio-geographical and socio-economic conditions of different areas, diverse sets of compounds can be used, resulting in entirely different pollution patterns. Due to specific climate, agriculture, industry and urbanization density of the Mediterranean region and the Iberian Peninsula as its representative, it is likely to expect distinct pollution of Mediterranean rivers compared to other geographical areas.

Moreover, chemicals that are being monitored on a regular basis are only a small fraction of all the chemicals present in the environment [9]. Many unregulated, emerging contaminants are being discovered which may have a significant impact on aquatic ecosystems and require special attention. Examples of compounds that have emerged recently as particularly relevant are pharmaceuticals and personal care products, polar pesticides, natural toxins, biocides, perfluorinated compounds, and nanomaterials [22]. Albeit, they are usually present in very low concentrations from pg/l to ng/l because of the improvement of analytical techniques, number and frequency of detections of emerging contaminants have increased [20]. Emerging environmental contaminants are not necessarily new chemicals, but the substances that have often been long time present in the environment and whose potentially adverse effects on human health and environment are only now being noted [23]. Thus, it becomes clear that it is necessary to evaluate the risk of emerging contaminants and if it is proven that some of them cause harmful effects to either, or both ecosystem and human health, to include them into the monitoring and regulation programs. Still, given the large number of chemical compounds released into the environment annually, it is not possible to conduct risk assessments for all emerging and existing chemicals. Moreover, not all the compounds that are present in the environment pose the significant risk to aquatic ecosystems or human health. This has led to the development of schemes for prioritizing compounds based on their potential risk in order to direct the monitoring efforts towards the important compounds only. The assessment of whether a particular compound is a pollutant is based upon an understanding of its exposure (i.e., its input, distribution and fate in a defined system) and of the effects that the compound has on organisms, including humans, due to its presence in the system [26]. A priority chemical is one that, because of its importance, however defined, should be examined with greater urgency and in preference to other chemicals.

One approach for identifying potentially dangerous compounds is long-term screening of the environment for a large set of chemicals together with an assessment of the potential toxicity of the observed concentrations, which can be done by using measured or predicted effect concentrations for standard test species [27].

Generally, the (eco)toxicity of a given pollutant is determined by standardized tests, with the use of selected model organisms and toxicity endpoints, such as lethality in algae, *Daphnia* sp. and fish so that different trophic levels are covered as recommended by the WFD [11]. It is important to note that, in nature, organisms are exposed not to isolated chemicals but to complex mixtures of many chemicals at different concentrations. The individual components might be present at concentrations too low to raise concern but additive or even synergistic effects may occur that may result in higher toxicity of single compounds [26]. The most frequently used concepts for mixture ecotoxicity prediction are *concentration addition* (CA) and *independent action* (IA). Both models are used to calculate mixture toxicity based on the toxicity and concentration of individual constituents of the mixture and assume that all the components of the mixture

affect the same endpoint. The CA model assumes that all compounds have similar modes of action, while the IA model assumes that components of the mixture affect different systems of the organism [2]. However, neither CA of IA takes into account possible synergistic and antagonistic effects of mixtures. In this work we review several prioritization schemes that included emerging contaminants into prioritization and are focused on the risk of organic chemicals to aquatic systems. We have highlighted the contaminants that were multiple proposed as important aquatic contaminants according to these prioritization schemes and conducted the prioritization exercise using those compounds as our "contaminant pool" for prioritization. Advantageously, *hazard quotients* (HQ) can be used to quantify risk and subsequently determine the rank associated to each pollutant. From the foregoing considerations, the aim of the present exercise can be summarized as follows to identify the priority compounds specific to the Mediterranean aquatic system and to compare them with those found in other rivers worldwide.

Review of selected prioritization schemes

Many schemes for prioritizing chemicals according to their importance as aquatic contaminants have been developed [14] and here are summarized in Table 1. Most of them are based on the PBT criteria of the chemical combined with a quantity of that chemical in the environment [14].

Common drawback to these schemes are that they use different preselected chemicals, different ranking criteria and in most cases subjective judgment to make the decision for pre selection of compounds or giving the specific weight to different criteria. In general, most of prioritization schemes follow the same order. The first step is the pre-selection of the chemicals for the prioritization. For the selection of chemicals it is important to identify the reasons for the prioritization. The pre-selection of chemicals may be done according to existing legislation and monitoring data or by identification of sources and pressures [22]. The second step involves the exposure and toxicity estimation. The exposure of each contaminant can be determined by the potential of its emission into the environment, emission data, its persistence in a given system, distance between source and potentially endangered recipients, mechanisms of transport, etc. The exposure can be determined on the basis of monitoring data (i.e., environmental occurrence data) [15]. In the case of lack of monitoring data, the exposure can be estimated in the predictive way by different models, which use the information about the chemical's production quantity, frequency of its release to the environment, and predictions of its persistence and mobility in the environment [6].

Considering prioritization for the purpose of environmental protection, the toxicity of the chemical is usually determined by in vivo toxicity tests for standard test species (algae, *Daphnia* sp. and fish). The concentration of the chemical that provokes harmful effect or lethality of test species is measured. The most common is the usage of the *half maximal effective concentration* (EC_{50}) or the *half lethal concentration* (LC_{50}) as indicators of acute toxicity. Acute toxicity tests measure the dose of chemical that, after short-term exposure,

Table 1. Prioritization schemes with focus on aquatic environment, adapted from [11]

Preselected compounds	Criteria	Results	Ref.
78 compounds of "high concern"	PBT properties; estimated exposure levels	Chlorpyrifos, ametryn, dichloufluanid, prometryn, chlorothalonil, cyanazine, trifluralin, atrazine…	[16]
100 pharmaceuticals, personal care products and endocrine disruptors	Occurrence; treatment in water treatment plants; ecological effects; health effects	Mestranol, bisphenol A, AHTN, TDIP, estrone, tri(2-butoxyethyl) phosphate, celestolide, ethylhexyl methoxycinnamate, musk xylene, musk ambrette, bezafibrate, propylparaben, linuron, HHCB, atorvastatin, lindane, 17β-estradiol, etc.	[17]
250 compounds (WFD, relevant substances for river Rhine, measured in Swiss waters)	Potential occurrence in the water phase	Pentachlorophenol, PFOA, PFOS, azithromycin, ofloxacin, clarithromycin, erythromycin, roxithromycin, fluconazole diatrizoate, pentachlorobenzene…	[18]
500 classical (WFD) and emerging organic contaminants	Frequency and extent of exceedance of PNEC (predicted no-effect concentration)	Diazinon, azoxystrobin, terbuthylazine, heptachlor endosulfan I, 4,4'DDD, diuron, DEHP, irgarol, 2,4'-DDD, alachlor, pyrene, endosulfan II, PCB-180, 4,4'-DDE, heptachlor epoxide B…	[3]
Chemicals of Japanese Pollutant Release and Transfer Register (PRTR)	Human health; environmental effects	Dichlorvos, arsenic, cobalt and berilyum compounds, disulfoton, fenitrothion, parathion, diazinon, antimony compounds, chlorpyrifos-methyl, etc.	[19]

provokes certain endpoint effect (mortality, immobility, growth stagnation, etc.) in the test species. Conversely, chronic toxicity data refer to the dose of the chemical that provokes certain effect in the species after longer time exposure. Chronic exposure is especially important when considering chemicals that are present in the environment in low concentrations like emerging contaminants. Some of the chemicals that are present in low concentrations in the environment might be very persistent or might have been introduced into environment continuously and may cause unexpected long term effects [1]. However, chronic toxicity data is less common. Hence, predictive methodologies can be used to estimate toxicity data gaps. Chemical toxicity can be estimated by the *quantitative structure-activity relationships* (QSARs) [21]. The last step includes procedures or models for calculating the comparable risk of chemicals and final ranking or grouping the chemicals according to their risk.

Methods

For this comparative prioritization exercise, by literature review of aforementioned prioritization works, we selected 22 compounds that were multiple proposed as important pollutants according to different prioritization schemes, as well as 15 new compounds of the WFD list of priority substances. Therefore the list of selected compounds contains both classical and emerging contaminants. For Northern Europe and the USA, the mean and maximum MEC of compounds in river water were collected from the literature: the Elbe, Wesee, Aller, and Ems Rivers [16], over 100 European rivers from 27 European Countries [19] and 139 streams across 30 states in North America [25]. For the Iberian rivers (Ebro and Llobregat) data were obtained from the SCARCE-Consolider project database and literature [5].

Ecotoxicity data for standard test species were obtained from EPA's (US Environmental Protection Agency) ECOTOX database and the Footprint Pesticide Properties Database, or in the case of lack of test data were estimated by ECOSAR™. In the case of multiple data for the same compound, the lowest toxicity values were used. Collected data are summarized in Table 2. The QSARs from ECOSAR are used for aquatic toxicity prediction based on the similarity of structures to chemicals for which the aquatic toxicity measured data exist. Toxicity estimations are based on mathematical relationships between the octanol-water partition coefficient (K_{ow}) values and the corresponding measured toxicity. Since 1981, the US EPA has successfully applied QSARs to predict the aquatic toxicity of new industrial chemicals in the absence of test data [24]. However, it needs to be taken into account that the toxicity of those compounds with few data available can be underestimated, which might lead to errors in this kind of comparative exercises.

Hazard quotients (HQ) have been calculated for three standard test species corresponding to three different trophic levels, as recommended by the WFD. HQ are defined as the ratio of predicted or measured environmental concentrations and their chronic toxicity, usually expressed as *non-observed effect concentrations* (NOEC) or *predicted no effect concentration* (PNEC) values [3,4,7]. When NOEC values were not available, EC50 or LC50 values from standard ecotoxicological tests can be used after correction by an assessment factor [11] intended to extrapolate from acute to chronic toxicity. For the calculation of HQ we used ratio of MEC and estimated PNEC values from acute data EC50 divided by an assessment factor of 1000 as recommended by WFD (Eq. 1).

$$HQi = \frac{MECi}{PNECi} \; ; \; PNECi = \frac{EC50i}{1000} \text{ or } \frac{LC50i}{1000} \quad \text{(Equation 1)}$$

By ranking the HQ we identify the most relevant pollutants for each trophic level and for Iberian rivers (with Ebro and Llobregat rivers as representatives) and for North American and North European rivers.

Results and Discussion

Environmental occurrence of selected compounds. The occurrence of selected compounds in water samples from the Iberian Peninsula (SCARCE-Consolider Project Database) and [5], North Europe [19,25] and USA [16] data are illustrated in Fig. 1 and Fig. 2. Of the selected compounds, perfluorooctane sulfonic acid (PFOS) has the highest concentrations in Iberian rives. It is followed by pesticide imazalil, which might be the consequence of its extensive use in Mediterranean agriculture as it is mostly used as citrus fungicide. Citrus fruits are one of the predominant crops grown in the Mediterranean coast of Iberian Peninsula. High levels of plasticizer bisphenol A are present, probably due to high industrialization of this area.

Two pharmaceuticals are found in high concentrations, anti-inflammatory diclofenac and antibiotic azithromycin. Considering the high concentrations of pharmaceuticals, it is possible to conclude that wastewater treatment plants are not efficient enough for the removal of pharmaceuticals

Table 2. Modeled (ECOSAR) and measured toxicity of selected compounds

Compound	CAS number	ECOSAR Acute toxicity- EC50 (mg/l)			TEST Acute toxicity-EC50 (mg/l)		
		Algae	*Daphnia*	Fish	Algae	*Daphnia*	Fish
Aclonifen	074070-46-5	1.075	1.815	1.852	0.47	1.2	0.67
Azithromycin	083905-01-5	1.874	3.023	18.822	1.971	3.066	19.827
Bifenox	042576-02-3	1.266	4.183	2.534	–	0.35	0.67
Bisphenol A	000080-05-7	1.331	5.237	1.284	2.7	7.75	4.6
Buprofezin	069327-76-0	273	1.525	2.172	2.1	0.42	0.33
Chlorothalonil	001897-45-6	6.503	4.624	6.982	0.007	0.028	0.008
Cyanazine	021725-46-2	0.121	30.167	44.869	0.2	42	4
Cybutryne	028159-98-0	0.025	3.682	2.123	0.001	5.3	0.75
Cypermethrin	052315-07-8	0.009	0.000835	0.00125	0.1	–	0.001
Diazinon	000333-41-5	1.372	0.00123	0.276	6.4	0.001	3.1
Dichlorvos	000062-73-7	2.01	0.03	14.811	5.8	–	0.1
Diclofenac	015307-86-5	41.41	25.754	37.655	–	22.43	–
Dicofol	000115-32-2	0.1	0.053	0.05	0.075	0.2	0.124
Dieldrin	000060-57-1	0.18	0.055	0.214	0,1	0.25	0.001
Endrin	000072-20-8	0.18	0.055	0.054	0.18	0.004	–
Erythromycin	000114-07-8	6.369	8.617	46.882	0.02	113.07	–
Estrone	000053-16-7	8.74	2.184	3.834	8.74	2.184	–
Fenitrothion	000122-14-5	2.845	0.002	0.544	0.495	0.007	1.3
Heptachlor	000076-44-8	0.102	0.023	0.022	0.027	0.078	0.007
Heptachlor epoxide	001024-57-3	0.483	0.34	0.353	200	0.24	0.02
HBCDD	025637-99-4	0.024	0.004	0.004	–	0.0032	–
Imazalil	035554-44-0	0.121	0.594	0.656	0.87	3.1	1.48
Lindane	000058-89-9	2.761	1.565	2.238	2.5	0.516	0.022
Linuron	000330-55-2	0.144	3.61	12.442	0.016	0.12	3
Methidathion	000950-37-8	1.051	0.004	2.851	–	0.006	0.001
Methoxychlor	000072-43-5	0.348	0.115	0.144	0.6	0.001	0.052
Parathionmethyl	000298-00-0	5.967	0.004	1.087	3	0.007	2.7
PFOS	001763-23-1	32.647	16.916	23.664	–	37.36	–
Prochloraz	067747-09-5	0.15	0.734	0.789	0.0055	4.3	1.5
Prometryn	007287-19-6	0.034	5.606	3.973	0.002	9.7	2.9
Pyrene	000129-00-0	0.656	0.287	0.386	0.015	0.004	–
Pyripoxyphene	095737-68-1	0.392	0.136	0.172	0.15	0.4	0.27
Quinoxyfen	124495-18-7	0.3	0.098	0.123	0.027	0.08	0.27
Terbutryn	000886-50-0	0.033	5.336	3.701	0.002	7.1	0.82
Trichlorfon	000052-68-6	0.11	0.041	19.951	10	–	0.7
Ethinyl estradiol	000057-63-6	3.671	0.98	1.296	0.84	–	–
Estradiol	000050-28-2	4.299	1.129	1.578	4.299	2.87	–
2,4' DDD	000053-19-0	0.232	0.019	0.087	0.232	–	–

(–): Data not available.

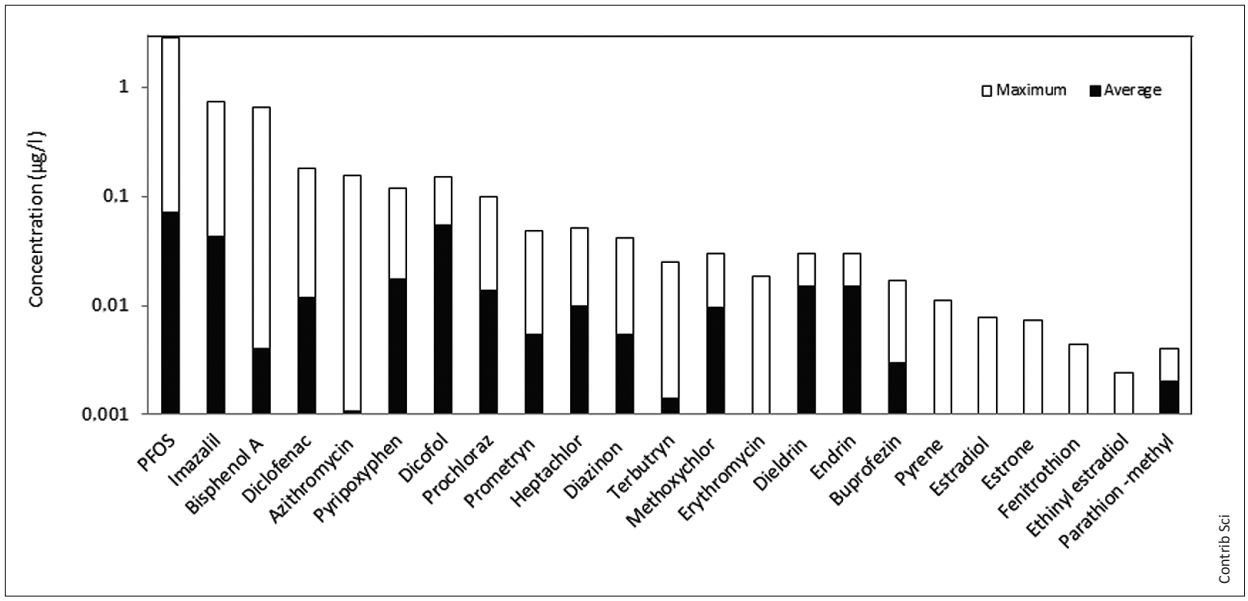

Fig. 1. Occurrence of selected compounds in Iberian rivers.

from the wastewater. Compared to other selected compounds, high concentrations of pharmaceutical erythromycin (1.71 µg/l) and hormone 17alpha-ethinylestradiol (0.831 µg/l) are measured in the USA river waters [16]. Overall, the differences observed in the occurrence of compounds confirm the need for area specific prioritization of potential pollutants.

Measured vs. modeled toxicity. Acute toxicity data of each compound for algae, *Daphnia* sp. and fish is presented in Table 2. In cases of lack of test data, toxicity was estimated by ECOSAR™ tool. Measured acute toxicity data were collected from open literature and compared to those modeled by ECOSAR™. The values of measured and modeled concentrations of selected compounds were proven to be in the

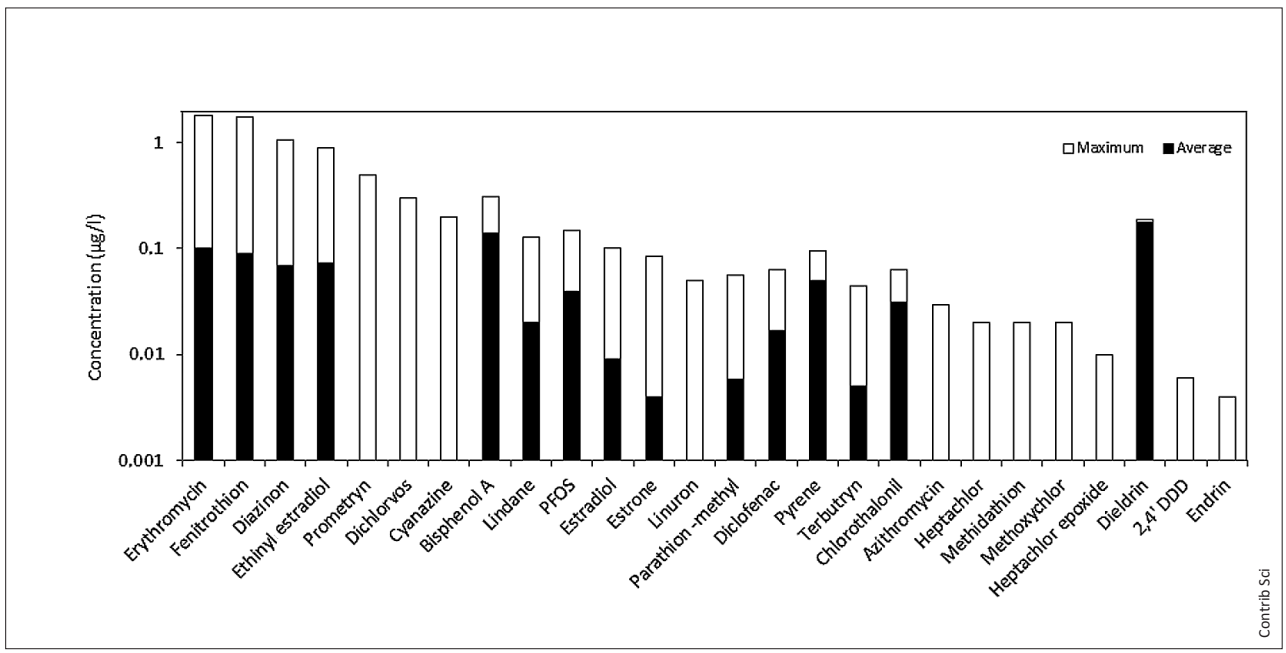

Fig. 2. Occurrence of selected compounds in USA and North European rivers.

Table 3. Ranked compounds according to HQ for algae, *Daphnia* sp. and fish in Iberian rivers

Rank	Compound	HQ Algae	Compound	HQ *Daphnia* sp.	Compound	HQ Fish
1	Prometryn	21.500	Diazinon	35.700	Dieldrin	15.000
2	Prochloraz	15.200	Methoxychlor	20.000	Heptachlor	5.8570
3	Terbutryn	11.700	Endrin	3.7500	Dicofol	0.7822
4	Heptachlor	1.5185	Pyrene	2.5750	Imazalil	0.4612
5	Dicofol	1.2933	Heptachlor	0.5256	Methoxychlor	0.3846
6	Erythromycin	0.9250	Fenitrothion	0.4900	Pyripoxyphen	0.3688
7	Imazalil	0.7847	Dicofol	0.4850	Endrin	0.2777
8	Pyrene	0.6866	Parathion-methyl	0.2857	Bisphenol A	0.1411
9	Pyripoxyphen	0.6640	Pyripoxyphen	0.2490	PFOS	0.1145
10	Bisphenol A	0.2405	Imazalil	0.2202	Prochloraz	0.0557
11	Dieldrin	0.1500	PFOS	0.1601	Buprofezin	0.0424
12	Endrin	0.0833	Bisphenol A	0.0838	Terbutryn	0.0285
13	PFOS	0.0829	Dieldrin	0.0600	Pyrene	0.0266
14	Azithromycin	0.0779	Azithromycin	0.0501	Prometryn	0.0148
15	Methoxychlor	0.0333	Buprofezin	0.0333	Diazinon	0.0115
16	Fenitrothion	0.0069	Prochloraz	0.0194	Azithromycin	0.0077
17	Buprofezin	0.0066	Diclofenac	0.0064	Estradiol	0.0049
18	Diazinon	0.0056	Prometryn	0.0044	Diclofenac	0.0044
19	Diclofenac	0.0039	Estrone	0.0033	Fenitrothion	0.0026
20	Ethinyl estradiol	0.0026	Terbutryn	0.0033	Estrone	0.0019
21	Estradiol	0.0018	Estradiol	0.0026	Ethinyl estradiol	0.0017
22	Estrone	0.0008	Ethinyl estradiol	0.0022	Parathion-methyl	0.0007
23	Parathion-methyl	0.0006	Erythromycin	0.0002	Erythromycin	0.0004

same orders of magnitude and therefore for this risk assessment and prioritization purpose both types of data were used.

Risk based prioritization. In general, HQ higher than 1 indicate potential risk. We used assessed chronic toxicity (PNEC) by applying an assessment factor of 1000 to EC_{50} or LC_{50} acute toxicity data as recommended by the WFD [11]. Before applying an assessment factor none of the compounds' HQ was higher than one. It must be taken into account that an assessment factor so high might lead to overstimation of risk. Also, we can conclude that acute risk from selected compounds is not likely due to low concentrations of these compounds. The results of chronic toxicity assessment show that, in Iberian rivers, hazard quotients higher than one are for 22% of selected compounds for algae, 17% for *Daphnia* sp. and 9% for fish (Table 3). However, other adverse properties (e.g., endocrine disruption, bioaccumulation, etc.) of chemicals besides their toxicity may be present but are not included in this kind of risk estimation. Comparing the risk expressed by HQ, the highest risk to algae, daphnia and fish is posed by pesticides, which are mostly on the top of the ranking list. The compounds that pose the highest risk for green algae are, as expected, herbicides (prometryn, terbutryn), fungicide (prochloraz), insecticides (heptachlor, dicofol). HQ of pesticide imazalil is ranked high on the list (HQ = 0.8) which might be the consequence of its extensive use in Mediterranean agriculture as citrus fungicide. The macrolide antibiotic erythromycin is following on the list. For *Daphnia* sp. and fish, erythromycin is found at the bottom of the ranking list. Diazinon, methoxychlor, endrin and pyrene are the compounds of potential risk for *Daphnia* sp., and insecticides

Table 4. Ranked compounds according to HQ for algae, *Daphnia* sp. and fish in North Europe and USA rivers

Rank	Compound	Algae	Compound	*Daphnia* sp.	Compound	Fish
1	Prometryn	250	Diazinon	1000.0	Methidathion	20.00
2	Erythromycin	85.00	Fenitrothion	242.85	Dieldrin	7.000
3	Terbutryn	20.00	Methoxychlor	20.00	Lindane	5.000
4	Chlorothalonil	4.714	Pyrene	11.50	Chlorothalonil	4.125
5	Fenitrothion	3.434	Dichlorvos	10.00	Dichlorvos	3.000
6	Linuron	3.125	Parathion-methyl	7.1429	Heptachlor	2.857
7	Pyrene	3.066	Methidathion	3.3333	Fenitrothion	1.307
8	Cyanazine	1.00	Chlorothalonil	1.1786	Ethinyl-estradiol	0.6412
9	Ethiny-lestradiol	0.9893	Endrin	1.0000	HepCl epoxide*	0.5000
10	Heptachlor	0.7407	Ethinyl-estradiol	0.8480	Methoxychlor	0.3846
11	Diazinon	0.1563	Linuron	0.4167	Diazinon	0.3226
12	Dieldrin	0.0700	2,4' DDD	0.3158	Prometryn	0.1724
13	Bisphenol A	0.0637	Heptachlor	0.2564	Pyrene	0.1192
14	Dichlorvos	0.0517	Lindane	0.2132	Endrin	0.0741
15	Lindane	0.0440	Prometryn	0.0515	2,4' DDD	0.0690
16	Methoxychlor	0.0333	HepCl epoxide*	0.0417	Estradiol	0.0589
17	2,4' DDD	0.0259	Estrone	0.0371	Cyanazine	0.0500
18	Endrin	0.0222	Estradiol	0.0324	Terbutryn	0.0488
19	Estradiol	0.0216	Dieldrin	0.0280	Bisphenol A	0.0374
20	Methidathion	0.0190	Bisphenol A	0.0222	Erythromycin	0.0363
21	Parathion-methyl	0.0167	Erythromycin	0.0150	Estrone	0.0211
22	Azithromycin	0.0147	Azithromycin	0.0095	Parathion-methyl	0.0185
23	Estrone	0.0093	PFOS	0.0065	Linuron	0.0167
24	PFOS	0.0034	Terbutryn	0.0056	PFOS	0.0046
25	Diclofenac	0.0011	Cyanazine	0.0048	Azithromycin	0.0015
26	HepCl epoxide*	0.0001	Diclofenac	0.0018	Diclofenac	0.0012

*Heptachlor epoxide.

such as dieldrin and heptachlor for fish. Pharmaceuticals diclofenac and azithromycin were also at the bottom of the lists for all three species. However, even though pharmaceuticals are designed to affect the human body or, in the case of veterinary use, animals, they might have unexpected effects to other species in the environment. Moreover, estrone and estradiol are ranked very low at all lists but it does not mean that they should be disregarded and declared as safe because

they are known to be endocrine disruptors and cause reproductive disruption in wild fish populations [12].

For the USA and North European rivers, compounds with HQ > 1 are having 31% of compounds for algae, 35% for *Daphnia* sp. and 27% for fish (Table 4). Pharmaceutical erythromycin ranks second on the list for algae. Different production volume and consumption of this pharmaceutical in the USA, compared to Spain, is the reason for the detection of higher concentrations of erythromycin in USA river water [16], which results in higher ranking according to its very high hazard quotient (algae HQ = 85) compared to Iberian Rivers (algae HQ = 0.925). Again, pesticides rank the highest for all three species, followed by pyrene and etinylestradiol due to its higher concentrations in river water in USA [16]. Imazalil, which is found in high concentration in Iberian rivers, was not evaluated for these rivers since no data regarding its occurrence were available. Herbicide linuron and fungicide chlorothalonil are two potentially dangerous compounds for algae in this group of rivers; however, data concerning their occurrence in Iberian rivers were lacking and therefore were not included in the evaluation for those rivers. The differences on the lists of ranked compounds are due to different occurrence patterns of compounds in those rivers.

Conclusions

Comparison between the occurrence of pollutants in Mediterranean (Iberian) and Northern Europe and USA rivers is not always possible because the lack of data for some compounds. From the data we compiled, differences are noticeable and might be explained in terms of different usages associated to certain specific economic activities, different treatment in wastewater plants, hydrogeochemistry of river water, hydrological regime (i.e., drought seasons), climatological conditions, land use differences etc. They result on specific lists of priority compounds that are relevant from the management point of view and must be taken into consideration in connection with the WFD implementation.

Homogenous experimental toxicity data for the same species, same test time and same endpoint were not always available. Modeled ECOSAR™ toxicity data were used in these cases. The comparison of modeled and measured data showed that the levels of measured and modeled concentrations are in the same order of magnitude and therefore for this risk assessment and prioritization purpose both types of data can be used.

Considering HQs, note that, in Iberian rivers, emerging contaminants pose similar risk to pesticides such as linuron, heptachlor or endrin, which are recognized pollutants and banned in many countries. In general, pesticides ranked the highest for all three test species and for both Iberian and USA and North European rivers.

Compounds of highest potential for causing toxic effects in case of algae were mostly herbicides and fungicides (prometryn, prochloraz, terbutryn, heptachlor and dicofol). For *Daphnia* sp., compounds with potential risk were: diazinon, methoxychlor, endrin and pyrene, and for fish, dieldrin and heptachlor. For the North European and USA rivers, the group results were different for several compounds. Pharmaceutical erythromycin ranked second for algae (HQ = 85), it did not show HQ > 1 for Iberian rivers (HQ = 0.93), but also ranked high compared to other compounds.

Acknowledgments. This study has been financially supported by the EU through the FP7 project GLOBAQUA (Grant Agreement No. 605629) and by the Spanish Ministry of Economy and Competitiveness [project Consolider-Ingenio 2010 SCARCE CSD2009-00065], and was partly supported by the Generalitat de Catalunya (Consolidated Research Group: Water and Soil Quality Unit 2009-SGR-965). M. Kuzmanovic acknowledges AGAUR fellowship from the Generalitat de Catalunya.

Competing interests. None declared.

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