Comparing Chemical and Ecological Status in Catalan Rivers: Analysis of River Quality Status Following the Water Framework Directive

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Abstract In Europe, diverse biological indices and metrics have been developed for ecological status assessment in rivers using macroinvertebrate, diatoms, macrophytes, and fish communities according to the Water Framework Directive (2000/60/EC). Additionally, priority and hazardous substances (pesticides, PAHs, heavy metals, chlorinated and non-chlorinated solvents, endocrine disruptors, etc.) must be analyzed using their environmental quality standards (EQS) according to the 2008/105/EC Directive. Chemical and biological elements have to be properly combined to set the final water quality status. We compare ecological and chemical status outputs in a Mediterranean watershed (the Catalan river basins, NE Spain), in order to provide useful information about the strengths and weaknesses of quality status classification in rivers.

A total of 367 sites with different sampling frequencies along the monitoring program period (for six following years) were used to determine the chemical and the ecological status in Catalan rivers. The results of the monitoring program carried out in Catalan rivers (2007–2009) show a higher percentage of nonfulfillment quality objectives due to ecological status rather than chemical status. A total of 144 river water bodies (39%) do not achieve the good biological quality according to the 2000/60/EC Directive, whereas 68 river water bodies (19%) do not achieve the EQS for priority and hazardous substances provided by the 105/2008/EC Directive (chemical status). Both chlorinated pesticides (mainly endosulfan, trifluralin, and

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hexachlorocyclohexanes) and endocrine disruptors (nonylphenols and octilfenols) are the main substances responsible for quality standard failures in Catalan rivers.

Some chemical values must be carefully considered, since they are found near the EQS and their threshold detection values. EQS values for some priority substances (mainly heavy metals and organic compounds) are extremely low, up to threshold detection levels, which make chemical results uncertain. Additionally, bad chemical status does not necessarily imply biological community damages, at least in short time. A total of 21 river water bodies (6%) showed priority substance concentrations over the EQS thresholds, whereas biological elements showed good quality. Biological indices based on community structure and composition cannot detect specific chemical alterations at very low concentrations. Complementary analysis for risk assessment using biomarkers, species sensitivity distribution toxicity test, or other emerging tools can provide additional information of possible coming problems, which should be considered for investigative monitoring.

Keywords Biological quality • Catalan rivers • Chemical status • Mediterranean area • Priority substances • Water Framework Directive

Contents

1 Introduction and Objectives

The publication of the Water Framework Directive (2000/60/EC) (WFD) by the European Parliament and Commission at the end of 2000, and the subsequent approved Priority Substances Directive (105/2008/EC), provided significant changes in the process of assessing water quality in the European aquatic ecosystems [1–3]. This challenge must be carried out by using a new monitoring program, which EU Member Estates are bound to apply since 2007, according to the WFD requirements. Water quality measurements using biological elements reach a legal status together with the chemical status. Both biological quality and priority substances must be taken into account to establish a comprehensive water status diagnostics in rivers. That is why, the selection of proper biological elements, and their quality indices and class boundaries, became fundamental elements, which can significantly affect the outcome classification [4]. Moreover, priority and hazardous substances (pesticides, PAHs, heavy metals, chlorinated and non-chlorinated solvents, endocrine disruptors, etc.) must be carefully analyzed using suitable methods for their environmental quality standards (EQS) (2009/90/EC Directive). Chemical and biological analysis must be finally combined to set the final water quality status, and results need to be easily interpretable in terms of both chemical and ecological status to define a suitable program of measures.

In Europe, diverse biological indices and metrics have been developed for water quality assessment in rivers [5–8], using macroinvertebrate (e.g., [9–12]), diatoms (e.g., [13, 14]), macrophytes (e.g., [15]), and fish communities (e.g., [16]). Biological indices have also been applied in Catalan rivers since long time ago, basically developed in research centers [17–20], and more recently applied by Water Authorities following the WFD requirements [21–23]. The assessment of biological quality in rivers has been developed and enriched by contributions of several research centers and water authorities in order to achieve the normative definitions of WFD and their compliance with a gradient stressor [24, 25]. Additionally, quality class comparisons between countries have been carried out in order to harmonize and intercalibrate the information obtained [26, 27]. Thus, biological elements and their indices allow a comprehensive procedure to assess the ecological integrity for quality status classification in rivers. However, the WFD requires additional analysis combining biological indices and the presence of priority and hazardous chemical substances (chemical status). The chemical and ecological combination is required to ensure correct diagnosis in order to protect water ecosystem damages.

Chemical status is essentially defined by the compliance with the established environmental quality standards (EQS). A total of 33 substances or groups of substances, the so-called Priority Substances (PS) and Priority Hazardous Substances (PHS), were firstly set out by 2455/2001/EC Decision, and later by 2008/105/EC Directive. The list of PS and PHS is the outcome of an extensive risk assessment study carried out by the Fraunhofer Institut (Schmallenberg, Germany), according to the so-called COMMPS (Combined Monitoring-based and Modeling-based Priority Setting Scheme) methodology [28, 29]. The COMMPS procedure aims to quantify the risk associated with the exposure of a given chemical making use of two kinds of data, named modeling-based and monitoring-based. This procedure establishes a ranking of chemical substances according to a risk priority index. The exposure index of a chemical substance is calculated using all its measured concentration values in every sampling site from those compiled throughout Europe, whereas the effect index calculation is carried out by direct and indirect effects on aquatic organisms (toxicity and potential bioaccumulation), as well as indirect effects on humans (carcinogenicity, mutagenicity, adverse effects on reproduction, and chronic effects). The ranked list of substances resulting from the COMMPS procedure was updated in two new studies carried out by using both modeling [30] and monitoring procedures [31]. Setting out EQS for the different PS and PHS is based on the consideration of the reported chronic and acute ecotoxicities at different trophic levels, using appropriate safety factors (Annex V of 2000/60/EC

Directive). Regarding some chemical elements, EQS values are often very strict, but they should be understood under a precautionary principle.

For all those aforementioned priority substances, the European Commission shall submit proposals to control the progressive reduction of discharges, and phase out emissions of PHS in the environment within the forthcoming 20 years. As a whole, all the foresaid required information is supported on the data supplied by the corresponding surveillance or operational monitoring programs that must be carried out by their respective water authorities.

This chapter attempts to compare ecological and chemical status outputs in a Mediterranean watershed (the Catalan river basins, NE Spain), in order to provide useful information about the strengths and weaknesses of quality status classification in rivers according to the WFD requirements (2000/60/EC Directive). The biological quality indices provide a final diagnosis based on the analysis of biological community structure and ecosystem function, whereas chemical analysis of priority substances provides an indirect diagnosis from a set of environmental quality standard thresholds (EQS) previously established according to toxicity test on biota. Therefore, there is an obvious need to compare and analyze the relationship between chemical and ecological status to enhance the output interpretation. The whole of the cases determining good ecological status do not necessarily agree with a good chemical status, and vice versa. Hence, differences need to be carefully analyzed to properly classify the river quality status.

2 Monitoring Program Carried Out in Catalan Rivers

2.1 Sampling Sites and Study Area

Catalan basins are located in NE. Spain (Catalonia), by the Mediterranean Sea. Water is managed by the Catalan Water Agency, which is under the authority of the Catalan Autonomous Government (Generalitat de Catalunya). Catalonia contains two main hydrographic areas: on the one hand, the Catalan River Basin District, composed by several small watersheds that completely drain in Catalonia (Llobregat, Ter, Muga, Daró, Fluvià, Francolí, Foix, Besòs, Gaià, Tordera, Riudecanyes, and several small coastal streams), and on the other hand, a part of the Ebro basin, a transboundary big basin which drains through several regions in Spain (Fig. 1). The Catalan Water Agency has full competences for managing water supply and restoring quality status in the Catalan River Basin District, whereas Catalan Water Agency only monitors and makes suggestions for water management in the interregional basin (the part of the Ebro basin located within Catalonia). Transboundary basins among regions are managed by the Spanish central government through water authorities called Hydrographic Confederations, one for each Basin District. Thus, the Ebro watershed is managed by the Ebro Hydrographic Confederation.

Fig. 1 The location in Europe and the boundaries of Catalonia (31,990 Km^2) are shown. The Catalan River Basin District, made up by several watersheds (in *gray*), is fully located in Catalonia and drains to the Mediterranean Sea. The rest of the Catalan region is part of the Ebro watershed (interregional basin)

The Catalan River Basin District occupies a total area of 16,423 km^2, representing 52% of the territory of Catalonia, and housing 92% of the Catalan population (6.8 million inhabitants). The interregional basins that flow in Catalonia (Ebro river and its tributaries) have a total area of 15,567 km^2, representing 48% of the Catalan territory, and housing the remaining 8% of the Catalan population (0.6 million inhabitants).

A total water of 3,123 hm^3 per year (equivalent to 100 m^3/s) is used in whole Catalonia. From that volume of water, 38% (1,186 hm^3 per year) comes from the Catalan River Basin District, while 62% (1,937 hm^3 per year) is drawn from the interregional basins (part of the Ebro watershed located in Catalonia). Urban usage, comprising household and industrial consumption, accounts for 27.4% of total withdrawals (856 hm^3 per year), while agriculture uses, including irrigation and livestock consumption, accounts for the remaining 72.6% (2,267 hm^3 per year). The percentage of use significantly varies between the Catalan River Basin District and the part of the Ebro basin located in Catalonia. Thus, urban and industrial use makes up for the majority of the Catalan River Basin District, representing 65% of total consumption, whereas agricultural use predominates in the interregional basin, which represents over 95% of the total water consumed [32].

Catalonia, and especially the Catalan River Basin District, is one of the most industrialized areas of Spain. Waste and leak discharges from industrial and urban activities, and specific mining wastes (e.g., salt wastes), severely impact downstream areas in the Catalan River Basin District. Therefore, source-point pollution from industrial areas is mainly found in the lower Llobregat (also affected by salt mine activities), Tordera, Besòs, and Francolí basins [33, 34], whereas rivers close to agricultural and irrigation areas, mostly located in the lower Ebro basin and its main tributaries (e.g., the lower Segre), are mostly affected by diffuse pollution, and meaningful concentrations of pesticides and nitrates can be found [33].

According to the river basin characterization carried out by the Catalan Water Agency [35], a total of 6,639 km of the river network was used to select water bodies in all the Catalan basins. A total of 367 river water bodies were set out (with an average of 18 km per water body), from which a total of 136 (37%) were identified under risk of not fulfilling WFD objectives due to relevant pressures from human activities. River monitoring procedure and its sampling frequencies were defined taking into account water bodies in risk, and at least one sampling site per water body was established. So, a total of 367 sites (Fig. 1), with different sampling frequencies along the monitoring program period (for 6 following years), have been used to determine the chemical and the ecological status in Catalan rivers. Data used in this work have been sampled from 2007 to 2009.

2.2 Quality Elements and Methods

Suitable Mediterranean type-specific indices for each biological quality element (BQE) required by the WFD were considered for the biological quality assessment in Catalan rivers (Table 1). Quality indices for each biological element and reference conditions, using diatoms, macroinvertebrates, and fish fauna, were previously selected considering river typology. Quality classes were later combined among BQEs using the "one out, all out" criteria in order to establish the final biological quality class [36]. This is a restrictive procedure since the worst biological quality item is used to set the final quality status.

Biological data (macroinvertebrate, diatom, and fish fauna) was obtained from spring samples (from April to June). Changes in biological community composition are often found along time in Mediterranean rivers [37], and samples need to be collected in the same period to avoid natural disturbances [38]. Samples were gathered following specific sampling protocols for macroinvertebrate, diatoms, and fish fauna (protocols are available in the Catalan Water Agency WEB page). The IBMWP [39] for macroinvertebrate, the IPS [13] for diatoms, and the IBICAT

Table 1 Chemical elements (priority and hazardous substances) analyzed, and biological indexes used by the monitoring program for quality status surveillance in Catalan rivers

Quality assessment	Quality elements or group of chemical substances used	Biological indices or chemical substances used for quality assessment
	Macroinvertebrates	IBMWP
Biological quality	Diatom	IPS
	Fish fauna	IBICAT
Chemical status (priority and hazardous substances)	Heavy metals (16) substances	Mercury, aluminum, antimony, arsenic, cadmium, cobalt, copper, chrome, bari, iron, manganese, molybdenum, nickel, lead, selenium, zinc
	Chlorinated and non-chlorinated solvents (30) individual substances or grouped substances	Benzene, chlorobenzene, ethylbenzene, xylenes, naphthalene, toluene, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,1-dichloroethylene, 1,1-dichloroethane, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2-dichloroethane, 1,2-dichloropropane, 1,2-dichlorobenzene, 1,3,5-trichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, bromodichloromethane, bromoform, chloroform, dibromochloromethane, dichloromethane, tetrachlorethylene, carbon tetrachloride, trichloroethylene, trichlorofluorometane, 1,2-dichloroetilene ($c + t$), 1,3-dichloropropene($c + t$)
	Chlorinated pesticides (25) individual substances or grouped substances	Pentachlorophenol, alachlor, endosulfan I, endosulfan II, endosulfan sulfate, heptachlor, heptachlor epoxide A, heptachlor epoxide B, lindane, a-hexachlorocyclohexane, pentachlorobenzene, hexachlorobutadiene, 2.4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE, 2.4'-DDT, 4,4'-DDT, aldrin, dieldrin, endrin, endrin ketone, hexachlorobenzene, isodrin, metolachlor.
	Other pesticides (triazines, organophosphates and miscellaneous) (16) individual substances or grouped substances	Chlorpyrifos, diazinon, azinphosethyl, ethion, fenitrothion, malathion, methylparathion, molinate, parathion, chlorfenvinfos (E + Z), atrazine, propazine, simazine, terbutryne, tertbutilazine, trifluralin.
	Polycyclic aromatic hydrocarbons (PAH) (7) individual substances or grouped substances	Anthracene, benzo(a)pyrene, benzo(b) fluoranthene, benzo(ghi)perilene, benzo (k)fluoranthene, fluoranthene, Indene (1.2.3)pyrene.
	Endocrine disruptors (3) individual substances or grouped substances	4-*tert*-octylphenol, 4-nonylphenol, brominated biphenyl ether

index for fish fauna [23] were used to calculate the quality class for each BQE. These indices mainly came from European projects [16, 25], and are commonly being applied in Spain since long time ago. The IBMWP and IPS indices were also analyzed in the European intercalibration process carried out by Mediterranean countries (Mediterranean Geographical Intercalibration Group: Med-GIG), and later adopted by the European Commission as WFD normative compliant. All these indices have been properly tested and they are well correlated with the stressor gradient for major human activity pressures [21]. Data of quality indices were standardized by calculating the EQR values (Ecological Quality Ratio) [26]. Values of each quality index were divided by reference values to obtain the EQR. Reference values were previously obtained by calculating the average for selected reference sites according to each river type. EQR values allow proper comparisons among quality indices and BQEs, and their later combinations.

A total of 97 priority substances and group of substances (isomers, metabolites, etc.) were analyzed in Catalan rivers (Table 1) using suitable standard procedures. Atomic fluorescence spectroscopy for mercury, inductively coupled plasma mass spectrometry for metals, headspace extraction procedure for solvent substances [40], solvent extraction with simultaneous derivatization for pentachlorophenol [41], and solid-phase stirred bar extraction [42] for the rest of organic compounds were used. All chemicals were also analyzed or confirmed using GC-MS according to the 2009/90/EC Directive. From these 97 substances and group of substances, 42 are included in the Annex I of the 105/2008/EC Directive, whereas 55 substances are not currently included in this Directive (Table 2), but they are required by Spanish-national laws or are likely to be found in Catalan rivers due to industrial or agricultural activities. Only substances and thresholds provided by the 105/2008 Directive (EQSs) were applied for chemical status assessment. Values of heavy metals (lead, cadmium, mercury, and nickel), chlorinated solvents, pesticides (chlorine, phosphorus, and triazine), polycyclic aromatic hydrocarbons, and endocrine disruptors (nonylphenols, octilphenols, and brominated diphenyl ether compounds) were analyzed and compared with the EQS provided by the directive. All other chemical elements are used to analyze their evolution along time and detect possible hot spots.

Table 2 Number of substances or group of substances measured by the Catalan Water Agency in the Monitoring Program carried out in Catalan rivers (2007–2009)

Group of compounds	Chemicals analyzed included in the 105/2008/EC Directive	Chemicals analyzed and not included in the 105/2008/EC Directive	Chemicals not analyzed and included in the 105/2008/EC Directive
Heavy metals	4	12	0
Solvents	8	23	0
Chlorinated pesticides	14	9	0
Others pesticides	6	11	3
PAH	7	0	0
Endocrine disruptors	3	0	2
Total	42	55	5

Five substances or group of substances included in the 105/2008/EC Directive (tributyltin compounds, diuron, isopropuron, Di(2-ethilhexil)phtalate (DEHP), and chloroalkanes) were not analyzed (Table 2). These elements require complex laboratory procedures and their analysis is difficult. Also some detection thresholds are not easy to be achieved and can provide misleading results. Quality thresholds provided by the 105/2008/EC Directive for some compounds (e.g., brominated diphenyl ether and tributyltin compounds) are extremely low.

2.3 Frequency and Monitoring Campaigns

The Catalan monitoring program is based on the combination of several frequencies depending on quality element and the risk classification of each water body (Table 3). Sampling sites belong to each risk category, and the number of performed samples in the monitoring program period is defined according to each biological and chemical element. The entire monitoring program is completed after 6 years. Notice that, for management purposes, the differentiation among types of monitoring is not as relevant as the need to optimize and efficiently allocate the available resources on a working calendar or schedule. Therefore, the problem to be solved by the Monitoring Program can be envisaged in a logistic perspective. A specific monitoring program adapted to each typology of water was designed, and it is carrying out by the Catalan Water Agency in Catalan rivers.

3 Data Analysis and Results

3.1 Biological Quality

A total of 145 water bodies (66% of water bodies with data available) achieve good quality according to the IPS index based on diatoms (Table 4). Diatoms are very

Table 3 Sampling frequency applied by the Monitoring Program for biological quality and chemical status assessment in Catalan rivers

Water body classification	Biological quality			Chemical status
	Macroinvertebrates	Diatoms	Fish fauna	Priority substances
With risk	6	3	2	72
Without risk	2	1	1	1
Reference	3	2	1	6

Sampling frequencies for each water body are classified according to its risk to not achieve the good status (previously analyzed using human pressures). Numbers in boxes refer to samples required within the 6 year period of whole monitoring program. Therefore, “6” means once a year, “1” once every 6 years, “3” once every 2 years, and “72” monthly samples

Table 4 Number of river water bodies classified in five biological quality classes for each biological quality element (diatoms, macroinvertebrate and fish fauna) in the Catalan River Basin District (RBD), the Ebro watershed located in Catalonia, and in whole Catalan rivers. Some water bodies were not sampled yet (basically headwaters without human pressures), and were considered without data

		Achieve biological quality		Do not achieve biological quality			
		High	Good	Moderate	Poor	Bad	Without data
Diatoms	Catalan RBD	39	43	33	21	10	102
	Ebro watershed	50	13	8	2	0	46
	All Catalan rivers	89	56	41	23	10	148
Macroinvertebrate	Catalan RBD	65	45	42	20	5	71
	Ebro watershed	53	25	8	1	0	32
	All Catalan rivers	118	70	50	21	5	103
Fish	Catalan RBD	52	29	21	17	23	106
	Ebro watershed	72	4	7	5	3	28
	All Catalan rivers	124	33	28	22	26	134
Biological quality	Catalan RBD	19	50	69	36	16	58
	Ebro watershed	44	23	18	4	1	29
	All Catalan rivers	63	73	87	40	17	87

sensitive organisms for organic pollution discharges and they have a rapid response to disturbances [13]. Therefore, low IPS index values are found near urban and industrial areas, mainly located in lower rivers (Fig. 2), where generally continuously high nutrient loads are received. Bad quality using IPS values is found in Besòs river, the lower Anoia, Llobregat, and Muga rivers, and from the middle Tordera until the mouth.

Meaningful differences are found between the Catalan River Basin District and the Ebro watershed located in Catalonia. Whereas 56% of water bodies with data available (82 water bodies) achieve the WFD objectives in the Catalan River Basin District, a total of 86% of water bodies with data available achieve the WFD objectives in Ebro basin.

Similar results, though a little bit more optimistic, are found using macroinvertebrates as a BQE (Fig. 3). Quality objectives (good and high quality) are achieved for 71% of water bodies with data available (188 water bodies) in all Catalan rivers (Table 4). Macroinvertebrates are also sensitive to organic pollution, but they have a slower and sustained response to disturbances than diatoms [7]. However, low IBMWP index values are quite consistent with diatoms results. The mid-Anoia river and lower Llobregat, Foix, Besòs, Tordera, and Muga rivers presented very low quality levels. Rivers located in the Ebro watershed show higher quality values; therefore high and good quality are achieved for a 90% of water bodies with data available (78 water bodies), whereas 62% (110 water bodies) are achieved in the Catalan River Basin District.

Fig. 2 Biological quality results using diatom communities (IPS index) in Catalan rivers (2007–2009). High quality is shown in *blue*, good quality in *green*, moderate quality in *yellow*, poor quality in *orange*, and bad quality in *red* color. Water bodies without data are shown in *gray* color. Reservoirs are shown in *light blue*

Fish fauna show the worst quality scenario from measured biological elements in Catalan rivers. A total of 67% of water bodies with data (157 water bodies) presented consistent fish communities dominated by native species in whole Catalan rivers (Table 4). However, this situation is very different between both water bodies located in the Catalan River Basin District and in the Ebro basins. Whereas 83% water bodies with data available (76 water bodies) achieve high and good quality in the Ebro watershed located in Catalonia, only a 57% of water bodies (81 water bodies) with data available achieve WFD objectives in the Catalan River Basin District. Fish fauna are sensitive to water pollution, but also to morphological and flow alterations, river discontinuity, and habitat lost. Low quality values using fish fauna denote lack of suitable hydrological conditions, and rivers located in the Catalan River Basin District are characterized by water scarcity, whence habitat

Fig. 3 Biological quality results using macroinvertebrate communities (IBMWP index) in Catalan rivers (2007–2009). High quality is shown in *blue*, good quality in *green*, moderate quality in *yellow*, poor quality in *orange*, and bad quality in *red* color. Water bodies without data are shown in *gray* color. Reservoirs are shown in *light blue*

alteration and water abstractions considerably affect native fish community composition. Moreover, also other threats such as exotic alien species invasions, basically due to fishing or other human activities, negatively affect fish communities and prevent from achieving a good biological quality. Llobregat and Ter basins show a high number of water bodies dominated by nonnative fish species (Fig. 4). The lower Ebro and Segre rivers (in the Ebro basin located in Catalonia) also show a high number of nonnative species.

Finally, high and good biological quality, combining macroinvertebrate, diatoms, and fish quality classes, are achieved in 49% of water bodies with data available (136 water bodies) in whole Catalan rivers (Table 4). Biological quality was determined using the worst three biological quality levels measured. Results show high and good quality in high mountain streams, basically rivers draining

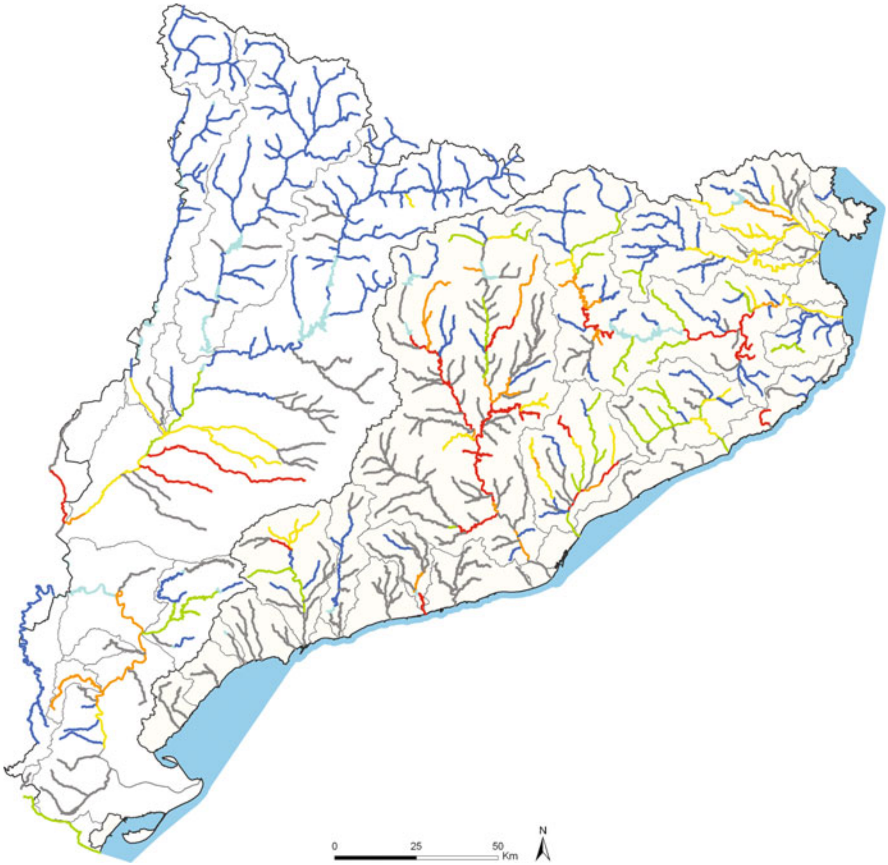

Fig. 4 Biological quality results using fish fauna (IBICAT index) in Catalan rivers (2007–2009). High quality is shown in *blue*, good quality in *green*, moderate quality in *yellow*, poor quality in *orange*, and bad quality in *red* color. Water bodies without data are shown in *gray* color. Reservoirs are shown in *light blue*

from the Pyrenees and protected areas, and small streams far from urban and agricultural areas, mostly tributaries of major rivers. The lower Besòs, Llobregat, Francolí, and Muga rivers, located close to urban and industrial areas, show many water bodies with bad or poor biological quality. Also, lower Segre river and its tributaries that flow between irrigation areas show bad and poor biological quality (Fig. 5). According to the diatoms, macroinvertebrate, and specially due to fish fauna, meaningful differences are found between the Catalan River Basin District and the Ebro watershed located in Catalonia. Whereas only 36% of water bodies with data available (69 water bodies) achieve the WFD objectives in the Catalan River Basin District, a total of 74% of water bodies with data available (67 water bodies) achieve the WFD objectives in the Ebro basin located in Catalonia.

Fig. 5 Biological quality results in Catalan rivers (2007–2009). High quality is shown in *blue*, good quality in *green*, moderate quality in *yellow*, poor quality in *orange*, and bad quality in *red* color. Water bodies without data are shown in *gray* color. Reservoirs are shown in *light blue*

3.2 Chemical Status

Quality standards provided by the 105/2008/EC Directive are achieved in a 75% of water bodies with data available (206 water bodies) in whole Catalan rivers (Table 5). A total of 68 water bodies do not achieve good chemical status in Catalan rivers. Unfulfilled quality standards are close to industrial areas basically located in the Catalan River basin District (lower Llobregat and Besòs rivers), and close to drainage irrigation fields located in the lower Segre river (in the Ebro watershed) (Fig. 6). Also, additional unfulfilled quality standards are found in some small streams located in the upper Segre watershed, draining from Pyrenees, although these values must be tentatively considered and require further validation.

Table 5 Number of river water bodies classified according to chemical status for each group of priority substances and group of substances (chlorinated pesticides, other pesticides, chlorinated and non-chlorinated solvents, endocrine disruptors, heavy metals, and polycyclic aromatic hydrocarbons) in the Catalan River Basin District (Catalan RBD), the Ebro watershed located in Catalonia, and in whole Catalan rivers. Some water bodies were not sampled yet (basically headwaters without human pressures), and were considered without data

		Achieve good status	Do not achieve good status	Without data
Heavy metals	Catalan RBD	170	11	67
	Ebro watershed	95	0	24
	All Catalan rivers	265	11	91
Chlorinated and non-chlorinated solvents	Catalan RBD	180	1	67
	Ebro watershed	95	0	24
	All Catalan rivers	275	1	91
Chlorinated pesticides	Catalan RBD	172	9	67
	Ebro watershed	67	28	24
	All Catalan rivers	239	37	91
Other pesticides	Catalan RBD	174	7	67
	Ebro watershed	86	9	24
	All Catalan rivers	260	16	91
Polycyclic aromatic hydrocarbons	Catalan RBD	181	0	67
	Ebro watershed	95	0	24
	All Catalan rivers	274	2	91
Endocrine disruptors	Catalan RBD	148	33	67
	Ebro watershed	93	2	24
	All Catalan rivers	241	35	91
Chemical status	Catalan RBD	145	36	67
	Ebro watershed	63	32	24
	All Catalan rivers	208	68	91

Chemical status results are analyzed for each different set of compounds (Table 5). Both chlorinated pesticides and endocrine disruptors are the main substances responsible of quality standard failures in Catalan rivers. Chlorinated pesticides do not achieve quality standards in 37 water bodies (a 13% of Catalan water bodies with data available), and they are mainly located in the Ebro watershed (lower Segre river close to irrigation areas). Mostly endosulfan, trifluralin, and also hexachlorocyclohexanes (lindane) are the main hazardous substances found over their EQS. Trifluralin is found in tributaries of lower Llobregat and Segre rivers with an average concentration of 0.05 μg/L (slightly over its EQS value: 0.03 μg/L). Lindane is found in nine water bodies, basically located near urban and industrial areas in Besòs and Llobregat rivers, and also close to agricultural zones in the lower Segre river, with an average value of 0.03 μg/L (EQS: 0.02 μg/L), and with a maximum value of 0.1 μg/L (EQS: 0.07 μg/L), whereas endosulfan (mainly endosulfan II) is broadly detected in some small tributaries draining from high mountains in the upper Segre watershed. Endosulfan is detected in 28 water bodies

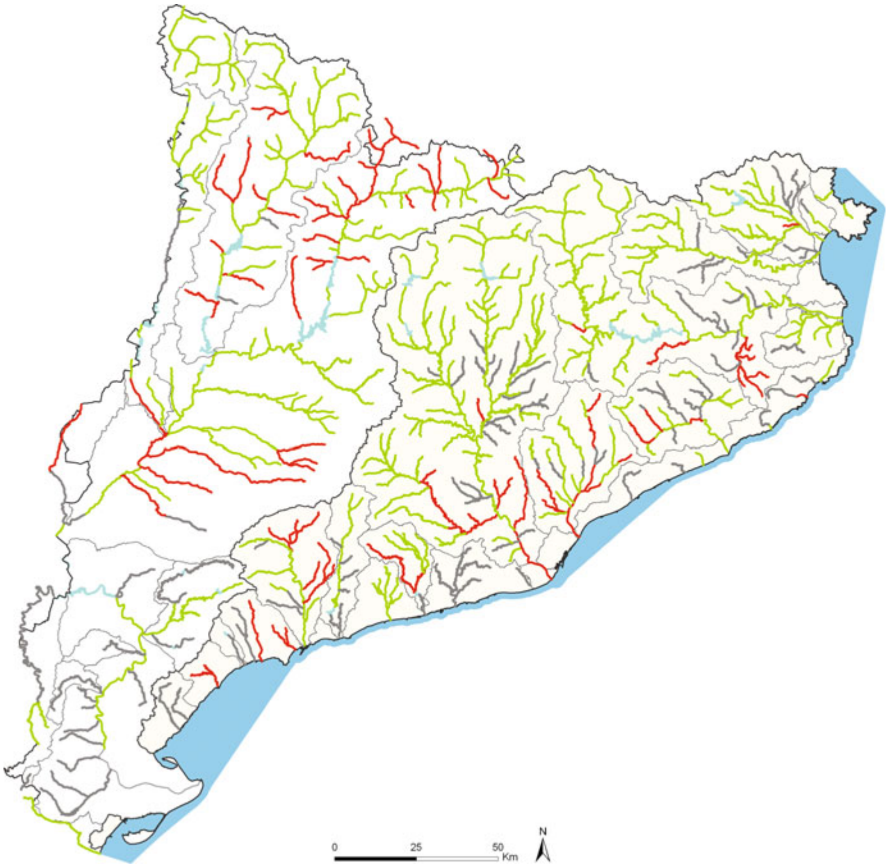

Fig. 6 Chemical status results in Catalan rivers (2007–2009). Good quality is shown in *green*, and bad quality in *red* color. Water bodies without data are shown in *gray* color. Reservoirs are shown in *light blue*

with an average value of 0.02 μg/L (EQS: 0.005 μg/L), with a maximum value of 0.3 μg/L (EQS: 0.01 μg/L). The origin of endosulfans found in the upper watershed area of Segre river is not clear. No relevant human activities, neither industrial nor significant agricultural uses, are located in this area, and data should be carefully considered. Similar concentrations and equivalent isomeric relationship have been reported for endosulfan substances in high mountain water bodies by other authors [43, 44] in the same region. Atmospheric deposition is envisaged as a possible source of endosulfan concentration detected in high mountain rivers and lakes, due to their higher proportion of β-isomer compared with the α-isomer found in those samples. The abundance of α-isomer of endosulfan gradually increases with respect to β-isomer in the atmosphere concentration according to the distance from the endosulfan source. So, endosulfan atmospheric composition is normally dominated by α-isomer. However, the highest volatility and lower water solubility of α-isomer can increase the β-isomer composition in rain deposition and its input in rivers [45, 46]. Endosulfan concentrations found in Catalan high mountain rivers need to be afterward monitored to properly set out their origin.

Regarding triazines, organophosphates, and miscellaneous compounds (named other pesticides in this manuscript), they do not achieve quality standards in 16 water bodies (6% of water bodies with data), basically located in the Ebro watershed (9 water bodies), although they can also be found in the Catalan River Basin District (7 water bodies). Chlorpyrifos, chlorfenvinfos, and simazine are the most detected compounds found in Catalan rivers. They are mainly found at low concentrations close to quality standard values provided by the 105/2008/EC Directive. Chlorpyrifos is found close to irrigation areas in the lower Segre river, and also in the lower Llobregat watershed, in 18 water bodies with an average concentration of 0.03–0.09 μg/L (EQS: 0.03 μg/L), whereas chlorfenvinfos and simazine are only located in two water bodies. Levels of chlorfenvinfos are detected at 0.1–0.15 μg/L (EQS: 0.1 μg/L) in lower Llobregat watershed, whereas simazine is also slightly detected at 1 μg/L (EQS: 1 μg/L) in the upper Francoli river. Most pesticides have been detected close to or slightly over the EQS values and their threshold detection. That is the reason why they must be tentatively considered and later evaluated over time to be confirmed.

Endocrine disruptors are mainly found in the Catalan River Basin District, close to industrial areas. A total of 35 water bodies do not achieve the quality standards in whole Catalan rivers, from which 33 are located in the Catalan River Basin District (in lower Llobregat and Besòs rivers). Nonylphenols (EQS: 0.3 μg/L) and octilfenols (EQS: 0.1 μg/L) are present in the wastewater mainly coming from industrial uses with an average concentration of 0.4–0.8 μg/L. Endocrine disruptors are mostly detected in industrialized and high populated areas of Besòs basin, and the lower Llobregat and Anoia rivers. Similar endocrine disruptors' concentrations have been found by other authors close to industrial areas, where several types of dissolvent or similar compounds are mainly used in industrial processes [47].

Regarding heavy metal concentrations, they are also mainly found near industrialized areas (Besòs basin, and the lower Llobregat river), and additionally in some specific places due to mine activity (e.g., Osor stream, tributary located in the mid Ter river). Nickel values are detected over the quality standard (EQS: 20 μg/L) in 8 water bodies located close to industrial zones, mainly in the Besòs river, the lower Llobregat river (close to Barcelona industrial area), and Onyar stream (tributary of the lower Ter river, located close to Girona industrial area), with an average value of 30 μg/L. Also values of cadmium (EQS: 0.08–0.2 μg/L) are slightly detected in two water bodies, in the Osor stream due a old mine activity, and in the mid-Tordera stream, with an average concentration of 0.15 μg/L, close to the EQS value and its threshold detection.

A total of 21 water bodies, 5.7% of whole water bodies in Catalan rivers, were diagnosed with a good biological quality, using diatoms, macroinvertebrate, and fish fauna quality indices (Table 1), but did not achieve good chemical status

Table 6 Number of water bodies (rivers) classified as good biological quality, but do not achieve good chemical status

	Good biological quality and bad chemical status	
	Number of water bodies	Percentage of total water bodies(%)
Catalan River Basins District	18	7.1
Ebro watershed in Catalonia	3	2.7
All Catalan rivers	21	5.7

according to the quality standards provided by the 105/2008/EC Directive (Table 6). Main water bodies with a bad chemical status but good biological quality were detected in small watersheds close to agricultural areas, basically located in the Catalan River Basin District. Water bodies were mainly impacted by triazines, organophosphates, and miscellaneous pesticides, as endosulfan and clorpyrifos with low concentrations.

4 Discussion and Conclusions

Results from the monitoring program carried out in Catalan rivers (2007–2009) show a higher percentage of nonfulfillment quality objectives due to ecological status rather than chemical status. A total of 144 river water bodies (39%) do not achieve the good ecological status according to the 2000/60/EC Directive, whereas 68 river water bodies (19%) do not achieve the EQS for priority and hazardous substances provided by the 105/2008/EC Directive (chemical status). This ratio (2:1) between the number of river water bodies which do not fulfill ecological status versus chemical status can be easily explained. Ecological status integrates the effects of a comprehensive range of pressures on aquatic ecosystems, which result in a complex impact assessment procedure using biological elements. Biological indices analyze changes in the function and the structure of aquatic ecosystems, which can be caused by hazardous chemical compounds, but also by several other pressures such as high organic matter or nutrient concentrations, hydrologic and morphology alterations, habitat lost, riparian vegetation damages, alien species invasions, etc. Furthermore, ecological status assessment covers cumulative impacts over time; that is why it shows an integrated measurement.

Several authors have found significant correlations between biological indices and chemical elements [21, 34], even with priority substances [48–50]. Therefore, a percentage of bad biological quality could be explained by chemical quality standard nonfulfillment. However, some sites with bad chemical status but good ecological status were also found in Catalan rivers. A total of 21 river water bodies (6% of total river water bodies) showed priority substance concentrations over the EQS thresholds provided by the 105/2008/EC Directive, whereas biological elements showed good quality. Biological indices based on community structure cannot detect specific chemical alterations at very low concentrations. EQS thresholds for some chemicals have been very restrictively set out, and low concentrations, even over the EQS thresholds, cannot affect the community structure and biological indices, at least to a short time [49, 50]. Some studies have found that general contaminants, as high salinity or nutrient concentrations, highly affect the biological structure and composition than priority substances [51]. Low priority substances concentrations, close to threshold detection and their EQS values, cannot be detected by using current biological indices. Traditionally, in Europe and other industrialized countries, biomonitoring of freshwaters has been based on community structure measures, richness, or sensitive taxa, mainly focused on diatom and macroinvertebrate communities [6, 7]. Thus, low persistent chemical concentrations or sudden inputs may be overlooked using standard biological indices provided according to the WFD (Annex V, 2000/60/EC) [51, 52]. Additional tools for risk assessment analysis (e.g., biomarkers) could be required in order to identify coming problems. In this case, a recent Marie Curie project (KeyBioeffects project) allows us to test a new risk assessment method in Catalan rivers in order to provide additional information and define possible hot spots for forthcoming quality problems [53].

Also, rivers with good chemical status should not be completely rejected for ecosystem risk assessment, and a complementary analysis could be suggested, even more when ecological measurements do not achieve a good status. A recent combined toxicity test analysis, using new tools through theoretical toxicity data on biota, was carried out in Catalan rivers [54]. This study showed that chemical elements found in Catalan rivers could potentially impact about 50% of biota in 90% of sites, and less than 10% of biota in 10% of sites. Potential effects on freshwater ecosystems of cumulative individual toxicants, or/and their mixtures, are higher than the effective nonachievement of quality standards for priority substances found. Moreover, some EQS thresholds for priority substances provided by the 105/2008/EC Directive are too low to be properly detected using standard procedures and laboratories submitted to a quality certification. For instance, brominated diphenyl ether and tributyltin quality standard thresholds are extremely low, and they are not easily achieved by standard methods without high costs and expensive specific equipment. Also, current European regulations have not clearly defined specific methods and right techniques to properly quantify some priority substances (e.g., Chloroalkanes $C_{10\text{-}13}$). The difficulty to properly reach some EQS thresholds for certain priority substances makes the chemical status classification uncertain, even more at low concentration values, close to threshold detection. Besides, not all possible hazardous substances that can potentially affect the ecological status are continuously analyzed. Therefore, additional tools can result in a very powerful risk assessment complement, which can be recommended to better evaluate the risk of chemicals in rivers with high human pressures (downstream industrial discharges or agricultural diffuse contamination sources).

As a conclusion, ecological status and chemical status must be properly combined for surveillance monitoring in river ecosystems. Ecological status offers a comprehensive quality assessment for the integrated aquatic ecosystem using the biological community structure analysis. Additionally, chemical status analyzing priority and hazardous compounds (pesticides, chlorinated and non-chlorinated solvents, PAHs, heavy metals, endocrine disruptors, etc.) must be considered and carefully combined with the ecological status output in order to completely diagnose ecosystem damages. Biological elements' response to a broad range of pressures, and specific chemical elements, could not be detected by biological indices (basically focused on structure at community level) at least in a short time. Therefore, both ecological and chemical status must be combined by selecting the worst quality class (using the "one out, all out" criteria) to properly classify the quality status in rivers. However, two things should be taken into account. (1) On the one hand, some chemical values must be carefully considered, even more when concentrations are found near the EQS and their threshold detection values. As we explained before, EQS values for some priority substances (mainly heavy metals and organic compounds) were extremely decreased by the new 105/2008/EC Directive, up to threshold detection levels. Those levels are set out under a precautionary principle according to several toxicity test on biota. However, the difficulty to reach such EQS levels by proper standard methods and suitably accredited laboratories makes those results uncertain. In these cases, results should be considered under a precautionary principle, and further analysis can be recommended in order to verify the bad chemical status. (2) On the other hand, good chemical and ecological status do not necessarily imply no risk for ecosystem damages. As we explained before, not all chemical and hazardous compounds are currently and continuously analyzed. Therefore, background concentrations (under the threshold detection), and/or emergent pollutants currently not taken into account, can potentially affect the water ecosystem and their biological communities. That is why, river sites under high human pressures, mainly close to industrial and heavily urbanized areas, or near agricultural activities, need to be additionally monitored in order to avoid ecosystem damages, evenly if good ecological status is found. Biological indices cannot detect some hazardous chemical compounds, even more at low concentrations. In this regard, complementary tools for risk assessment using biomarkers, species sensitivity distribution toxicity test, or other emerging analysis can provide additional information of possible coming problems, which should be considered for investigative monitoring.

References

1. Allan IJ, Vranaa B, Greenwooda R, Millsb GA, Knutssonc J, Holmbergd A, Guiguese N, Fouillace AM, Laschif S (2005) Strategic monitoring for the European water framework directive. Trends Anal Chem 25(7):704–715
2. Bloch H (1999) European water policy facing the new millennium: the water framework directive. Assessing the ecological integrity of running waters. Vienna, Austria, pp 9–11
3. Coquery M, Morin A, Bécue A, Lepot B (2005) Priority substances of the European Water Framework Directive: analytical challenges in monitoring water quality. Trends Anal Chem 24 (2):117–127

4. Irvine K (2004) Classifying ecological status under the European Water Framework Directive: the need for monitoring to account for natural variability. Aquat Conservat Mar Freshwat Ecosyst 14(2):107–112
5. Carsten von der Ohe P, Prüß A, Schäfer RB, Liess M, de Deckere E, Brack W (2007) Water quality indices across Europe, a comparison of the good ecological status of five river basins. J Environ Monit 9:970–978
6. Hellawell JM (1986) In: Mellanby K (ed) Biological indicators of freshwater pollution and environmental management. Elsevier, London, p 546
7. Hering D, Johnson R, Kramm S, Schmutz S, Szoszkiewicz K, Verdonschot PFM (2006) Assessment of European streams with diatoms, macrophytes, macroinvertebrates and fish: a comparative metric-based analysis of organism response to stress. Freshwat Biol 51(9):1757–1785
8. Johnson R, Hering D (2010) Spatial concurrency of benthic diatom, invertebrate, macrophyte, and fish assemblages in European streams. Ecol Appl 20(4):978–992
9. Bonada N, Prat N, Resh VH, Statzner B (2006) Developments in aquatic insect biomonitoring: a comparative analysis of recent approaches. Annu Rev Entomol 51:495–523
10. Cairns J, Pratt JR (1993) A history of biological monitoring using benthic macroinvertebrates. In: Rosenberg DM, Resh V (eds) Freshwater biomonitoring and benthic macroinvertebrates. Chapman and Hall, New York, pp 10–27
11. Metcalfe JL (1989) Biological water quality assessment of running waters based on macroinvertebrates communities: history and present status in Europe. Environ Pollut 60:101–139
12. Sandin L, Hering D (2004) Comparing macroinvertebrate indices to detect organic pollution across Europe: a contribution to the EC Water Framework Directive intercalibration. Hydrobiologia 516(1–3):55–68
13. Kelly MG, Cazaubon A, Coring E, Dell'Uomo A, Ector L, Goldsmith B, Guasch H, Hürlimann J, Jarlman A, Kawecka B (1998) Recommendations for the routine sampling of diatoms for water quality assessments in Europe. J Appl Phycol 10(2):215–224
14. Prygiel J, Coste M, Bukowska J (1999) Review of the major diatom-based techniques for the quality assessment of rivers – State of the art in Europe. Agence de l'eau Artois Picardie, pp 224–238
15. Szoszkiewicz K, Ferreira T, Korte T, Baattrup-Pedersen A, Davy-Bowker J, O'Hare M (2006) European river plant communities: the importance of organic pollution and the usefulness of existing macrophyte metrics. Hydrobiologia 566(1):211–234
16. Pont D, Hugueny B, Rogers C (2007) Development of a fish-based index for the assessment of river health in Europe: the European Fish Index. Fish Manage Ecol 14(6):427–439
17. Muñoz I, Prat N (1994) A comparación between different biological water quality indexes in the Llobregat Basin (NE Spain). Ver Int Verein Limnol 25:1945–1949
18. Prat N (1991) Present trends in river studies. Oecol Aquat 10:1–12
19. Prat N, Rieradevall M (2006) 25-years of biomonioring in two mediterranean streams (Llobregat and Besòs basins, NE Spain). Limnetica 25(1–2):541–550
20. Sabater S, Guasch H, Picon A, Romaní A, Muñoz I (1996) Using diatom communities to monitor water quality in a river after the impllementation of a sanitation plan (river Ter, Spain). In: Proceedings of an International Symposium held at the Volksbildugsheim Grillhof, Austria (17-19 September 1995). Whiton BA, Rott E (eds) Use of algae for monitoring rives II, pp 97–103
21. Munné A, Prat N (2009) Use of macroinvertebrate-based multimetric indices for water quality evaluation in Spanish Mediterranean rivers. An intercalibration approach with the IBMWP index. Hydrobiologia 628:203–225
22. Munné A, Prat N (2011) Effects of Mediterranean climate annual variability on stream biological quality assessment using macroinvertebrate communities. Ecol Indic 11:651–662
23. Sostoa A, Casals F, Caiola NM, Vinyoles D, Sánchez S, Franch C (2003) Desenvolupament d'un índex d'integritat biòtica (IBICAT) basat en l'ús dels peixos com a indicadors de la qualitat ambiental dels rius a Catalunya. Documents tècnics de l'Agència Catalana de l'Aigua, p 203

24. Buffagni A, Erba S (2004) A simple procedure to harmonize class boundaries of European assessment systems. Discussion paper for the Intercalibration process – WFD CIS WG 2.A ECOSTAT, 6 February 2004, p 21
25. Buffagni A, Erba S, Birk S, Cazzola M, Feld C, Ofenbock T, Murray-Bligh J, Furse MT, Clarke R, Hering D, Soszka H, Van de Bund W (2005) Towards european inter-calibration for the water framework directive: procedures and examples for different river types from the E.C. project STAR, 11th STAR deliverable. STAR contract No: EVK1-CT 2001–00089. Rome (Italy). Quad Ist Ric Acque 123, Rome (Italy), IRSA, p 460
26. Heiskanen AS, Van de Bund W, Cardoso AC, Noges P (2004) Towards good of ecological status of surface waters in Europe – interpretation and harmonisation of the concept. Water Sci Technol 49:169–177
27. Pollard P, van de Bund W (2005) Template for the development of a boundary setting protocol for the purposes of the intercalibration exercise. Agreed version of WG 2.A Ecological Status. Version 1.2. 6 June 2005, Ispra, p 24
28. CEC (1999) Revised proposal for a list of priority substances in the context of the water framework directive (COMMPS procedure). Fraunhofer-Institut Umweltchemie und Ökotoxicologie. 98/788/3040/DEB/E1
29. Teixidó E, Terrado M, Ginebreda A, Tauler R (2010) Quality assessment of river waters using risk indexes for substances and sites based on the COMMPS procedure. J Environ Monit 12:2120–2127
30. Daginus K, Gottardo S, Mostrag-Szlichtyng A, Wilkinson H, Whitehouse P, Paya-Perez A, Zaldívar JM (2010) A modelling approach for the prioritisation of chemicals under the water framework directive. European Commission – Joint Research Centre, Italy; Environment Agency, UK. EUR 24292 EM
31. James A, Bonnomet V, Morin A, Fribourg-Blanc B (2009) Implementation of requirements on Priority Substances within the context of the Water Framework Directive. Prioritisation process: Monitoring-based ranking. Contract Nº 07010401/2008/508122/ADA/D2
32. ACA – Catalan Water Agency (2009) Pla de Gestió del Districte de Conca Fluvial de Catalunya (Catalan River Basin District Management Plan). Memòria, p 393
33. ACA – Catalan Water Agency (2010) Estat de les Masses d'Aigua a Catalunya 2007–2009. Resultats del Programa de Seguiment i Control. Barcelona, p 65
34. Prat N, Munné A, Rieradevall M, Solà C, Bonada N (1999) La qualitat ecològica del Llobregat, el Besòs, el Foix i la Tordera. Informe 1997. Estudis de la qualitat ecològica dels rius. 7. p 154. Àrea de Medi Ambient de la Diputació de Barcelona.
35. ACA – Catalan Water Agency (2005) Caracterització de les masses d'aigua i anàlisi del risc d'incompliment dels objectius de la Directiva Marc de l'Aigua (2000/60/CE) a Catalunya. Agència Catalana de l'Aigua. Departament de Medi Ambient i Habitatge de la Generalitat de Catalunya. Octubre, 2005, p 860
36. European Commission (2003) Overall approach to the classification of the ecological status and ecological potential. Water Framework Directive. Common Implementation Strategy. Working Group 2A. Ecological Status (ECOSTAT). 27 Nov 2003, p 47
37. Williams DD (2006) The biology of temporary waters. Oxford University Press, New York, p 337
38. Sporka F, Vlek HE, Bulánková E, Krno I (2006) Influence of seasonal variation on bioassessment of streams using macroinvertebrates. Hydrobilologia 566:543–555
39. Alba-Tercedor J, Jáimez-Cuéllar P, Álvarez M, Avilés J, Bonada N, Casas J, Mellado A, Ortega M, Pardo I, Prat N, Rieradevall M, Robles S, Sáinz-Cantero CE, Sánchez-Ortega A, Suárez ML, Toro M, Vidal-Albarca MR, Vivas S, Zamora-Muñoz C (2004) Caracterización del estado ecológico de los ríos mediterráneos ibéricos mediante el índice IBMWP (antes BMWP'). Limnetica 21(3–4):175–185
40. UNE-EN ISO 10301 (1997) Water quality. Determination of highly volatile halogenated hydrocarbons. Gas-chromatographic methods

41. Lee H, Weng L, Chau AS (1984) Chemical derivatization analysis of pesticides residues. VIII. Analysis of 15 chlorophenols in natural water by in situ acetylation. J Assoc Off Anal Chem 67 (4):789–794
42. León VM, Llorca-Pórcel J, Álvarez B, Cobollo MA, Muñoz S, Valor I (2006) Analysis of 35 semivolatile compounds in water by stir bar sorptive extraction-thermal desorption-gas chromatography–mass spectrometry. Part II: Method validation. Anal Chim Acta 558:261–266
43. Grimalt JO, Vilanova R, Fernández P, Martínez C (2001) Organochlorine pollutants in remote mountain lake waters. J Environ Qual 30:1286–1295
44. Grimalt JO, Fernández P, Carrera G (2002) Atmospheric deposition of organochlorine compounds to remote high mountain lakes of Europe. Environ Sci Technol 36:2581–2588
45. Shen L, Wania F (2005) Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. J Chem Eng Data 50:742–768
46. Weber J, Halsall CJ (2006) Endosulfan and ç-HCH in the Arctic: an assessment of surface seawater concentrations and air-sea exchange. Environ Sci Technol 40:7570–7576
47. Barceló D, Petrovic M (2007) Under the analytical spotlight, contaminants emerge: Report on the 2nd EMCO Workshop. Emerging contaminants in wastewaters: monitoring tools and treatment technologies. Belgrade (Serbia), 26 and 27 April 2007. Trac-Trends Anal Chem 26:647–649
48. Ginebreda A, Muñoz I, López de Alda M, Brix R, López-Doval J, Barceló D (2010) Environmental risk assessment of pharmaceuticals in rivers: relationships between hazard indexes and aquatic macroinvertebrate diversity indexes in the Llobregat river (NE Spain). Environ Int 36:153
49. Ricart M, Guasch H, Barceló D, Brix R, Conceição MH, Geiszinger A, López de Alda MJ, López-Doval JC, Muñoz I, Postigo C, Romaní AM, Villagrasa M, Sabater S (2010) Primary and complex stressors in polluted Mediterranean rivers: pesticide effects on biological communities. J Hydrol 383(1–2):52–61
50. Ricart M, Guasch H, Barcelo D, Brix R, Conceicao MH, Geiszinger A, de Alda MJL, Lopez-Doval JC, Munoz I, Postigo C, Romani AM, Villagrasa M, Sabater S (2010) Primary and complex stressors in polluted mediterranean rivers: pesticide effects on biological communities. J Hydrol 383:52–61
51. Damásio J, Taulera R, Teixidó E, Rieradevall M, Prat N, Riva MC, Soares A, Barata C (2008) Combined use of Daphnia magna in situ bioassays, biomarkers and biological indices to diagnose and identify environmental pressures on invertebrate communities in two Mediterranean urbanized and industrialized rivers (NE Spain). Aquat Toxicol 87(4):310–320
52. Damásio JB, Barata C, Munné A, Ginebreda A, Guasch H, Sabater S, Caixach J, Porte C (2006) Comparing the response of biochemical indicators (biomarkers) and biological indices to diagnose the ecological impact of an oil spillage in a Mediterranean river (NE Catalunya, Spain). Chemosphere 66(7):1206–1216
53. Carafa R, Real M, Munné A, Ginebreda A, Guasch H, Tirapu L (2010) Recommendations for Water Monitoring Programs of priority and emerging pollutants. Contribution from newly developed methods. KEYBIOEFFECTS project: cause-effect relations of key pollutants on the biodiversity of European rivers, p 67
54. Carafa R, Fanggiano L, Real M, Munné A, Ginebreda A, Guasch H, Flo M, Tirapu L, Carsten von der Ohe P (2011) Water toxicity assessment in Catalan rivers (NE Spain) using Species Sensitivity Distribution and Artificial Neural Networks. Science of the Total Environmental 409:4269–4279