SOCOPSE

SOURCE CONTROL OF PRIORITY SUBSTANCES IN EUROPE

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SOCOPSE
Source Control of Priority Substances in Europe

Specific Targeted Research Project

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Report on Ter and Llobregat case study

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1. Introduction

The aim of the Water Policy Framework Directive (WFD, 2000/60/EC) is to guarantee the good status of water systems, in terms of both quantity and quality, by means of the sustainable use of water based on the long-term preservation of water resources. Therefore new strategies are needed for control of Priority Substances (PSs). For decision making and implementation of the directive, the industrial sector, local water authorities and EU policy makers need guidelines for the selection and introduction of feasible and cost-effective measures.

In the framework of SOCOPSE Project, a decision support tool has been developed. The decision support system (DSS) consists of seven different steps to support the process of decision making. Thus, the purpose of the present document is to evaluate the DSS by applying to Ter/Llobregat case study (Spain). The PSs selected were: Atrazine, [Di(2-ethylexyl)-phthalate] (DEHP), Isoproturon, Hexachlorobenzene (HCB), Nonylphenol and PBDEs.

2. Step 0. System definition

2.1. Geographical Boundaries

The rivers Ter and Llobregat are covered by this case study. Both rivers belong to internal basin of Catalonia (Spain) and occupied a half of their surface (Figure 1).

Figure 1. Ter and Llobregat basin distribution.

Llobregat River covers 156 Kms long across populated and agriculturally intensive areas. The mean flow is around 22.2 m^3/s. On the other hand, Ter River flows 208 Kms to its mouth in the Mediterranean Sea. This basin long through an agriculturally intensive areas with a mean flow of 26.8 m^3/s. From the hydrological point of view, both rivers have a typical Mediterranean regime, characterized by high flow variability, which is mainly controlled by the seasonal rainfall. Some other characteristics of both rivers are listed in Table 1.

Table 1. Llobregat and Ter rivers main properties.

	Llobregat	**Ter**
Basin Area (Km^2)	4 957	2 955
Source Altitude (m)	1 259	2 480

Rainfall (mm/year)	672	879

2.2. General

Besides being a predominantly agricultural basin, human pressure on the Ter River is diverse and has increased in recent times. Intensive farming, urban development and industry depend on its waters. The main tributaries of river Ter are Freser River and Onyar River.

In the case of Llobregat River, during the last decades this river has been highly polluted by industrial and urban wastewaters, and by surface runoff from agricultural areas. The Llobregat River has two main tributaries, the Cardener River and the Anoia River. The occurrence of natural salt formations and the corresponding mining exploitations in the basin (Cardona, Suria and Sallent mining sites), have caused an increase in the salinity of the water.

Climate differs between the headwaters and the middle and lower parts of the catchments. Headwaters have an alpine influence with cold winters and mild summers, and annual rains ranging from 1000 to 1500 mm. In upland sub-basins, fluctuations in water discharge due to the Mediterranean climate create variable conditions in the rivers (Figure 2). Summer is usually very dry period while high discharge, due to heavy rain is common in autumn.

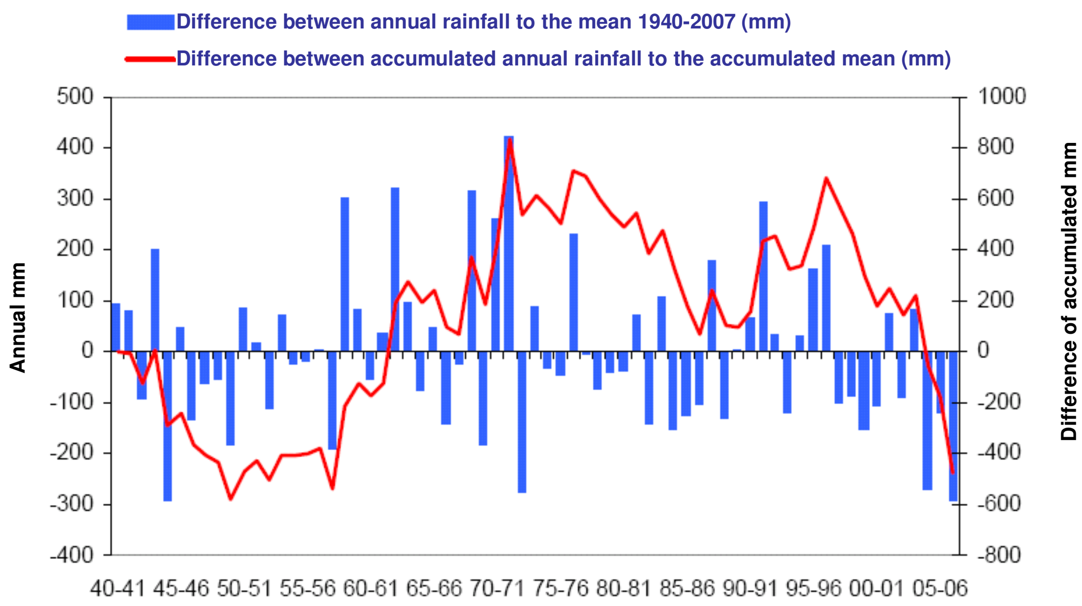


Figure 2. Mean annual rainfall in the Internal basins of Catalonia and differences between its accumulated value and mean accumulated value.

The rivers Ter and Llobregat, together supply drinking water to the metropolitan regions of Barcelona and Girona, which are home to 5.5 million people. The water supply drawn from the Ter (200 hm^3/year) and the Llobregat (160 hm^3/year) is supplemented by numerous, smaller groundwater sources, operated at a municipal level (Figure 3). This system is highly vulnerable in terms of guaranteeing supply as the quantity of water available is scant, at a level close to that of demand, while the reservoirs can only regulate demand for one year.

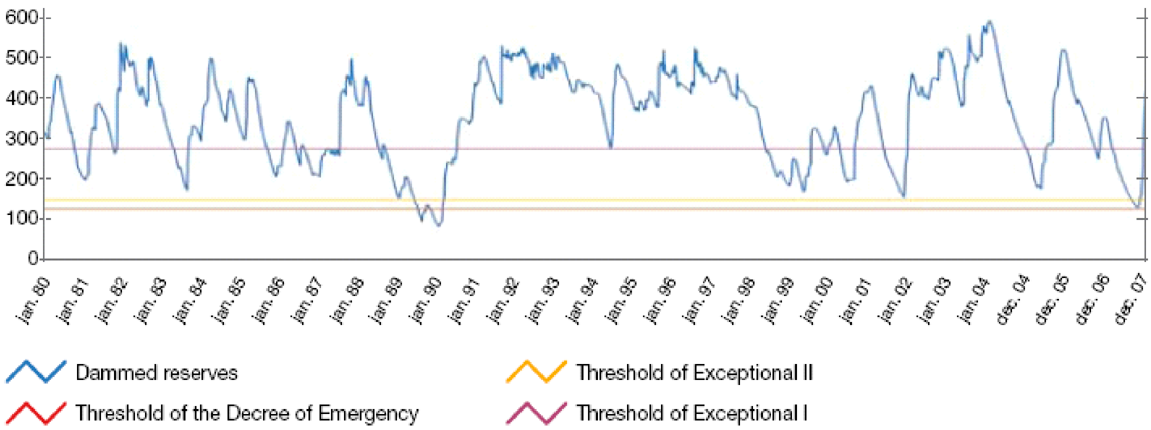


Figure 3. Dammed volumes in the Ter-Llobregat system.

2.3. Stakeholders and decision makers

The stakeholders involved are:

- Aigües Ter Llobregat (ATLL)
- Aigües de Barcelona (AGBAR)
- Centro Tecnologico del agua (CETAQUA)
- Agencia Catalana del Agua (ACA)
- Departament d'Agricultura , Alimentació i Acció Rural

2.4. Selected Substances

The included substances in the case study are:

- Atrazine

- Isoproturon
- Polybrominated biphenylethers (PBDEs)
- Nonylphenol (NP)
- Di(2-ethylhexyl)-phthalate (DEHP)

3. Step 1. Problem definition

3.1. Data sources

The environmental data mainly came from ACA's screening and monitoring programs for the correct implementation of WFD in Catalonia (Figure 4). All these data are available in the website of the agency (http://aca-web.gencat.cat/aca/appmanager/aca/aca/)

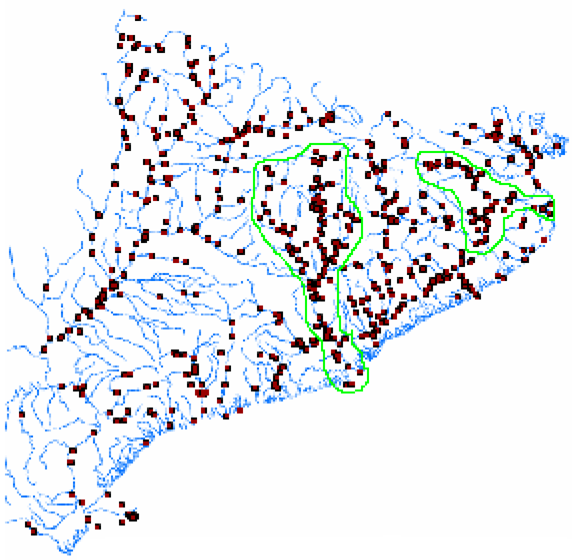


Figure 4. Superficial quality control network in Catalonia (ACA).

More data were obtained from other studies, such as works carried out in the framework of another European project: Models for assessing forecasting the impact of environmental key pollutants on marine and freshwater ecosystem and biodiversity (MODELKEY, GOCE511237).

Furthermore, extra data were obtained from emissions of WWTP analyzed by ACA in fulfilment of European Pollution Release and Transfer Register (EPTR, Regulation 166/2006).

3.2. Result of the step

The main problems for Llobregat and Ter river basin are listed in Table 2. For Llobregat River the most important problem is the industrial and urban contamination. On the other had, for Ter River the agriculture contamination is an important factor to keep in mind.

Table 2. Pollution problems in Ter and Llobregat rivers.

<table>
<tr><th>Llobregat</th><th>Ter</th></tr>
<tr><td>Industrial and urban contamination</td><td>Agriculture contamination (nitrate, pesticides) of ground water</td></tr>
<tr><td>Salt Mining</td><td>Hydropower plants: Ecological flow alteration</td></tr>
<tr><td>Hydropower plants: Ecological flow alteration</td><td>Water abstraction</td></tr>
<tr><td>Ground water overexploitation and contamination</td><td rowspan="2">Ecosystem preservation</td></tr>
<tr><td>Water abstraction</td></tr>
</table>

In fulfilment of WFD, ACA gathers data obtained from regular monitoring of the quality control network (survey, operational and investigative monitoring). In Table 3 and Table 4 are summarized the data obtained for Llobregat and Ter rivers, respectively. The PSs concentrations are compared with the Environmental Quality Standards (EQS), according to Directive 2008/105/EC.

Table 3. PSs studied concentration in the Llobregat River (2004-2008).

Substance	ng/L		ng/L	
	min	max	AA-EQS	MAC-EQS
Atrazine	2	94	600	2000
penta-BDE	n.a.	n.a.	0.5	n.a.
DEHP	n.a.	n.a.	1300	n.a.
Hexachlorobenzene	0.1	2.5	10	50
Isoproturon	n.a.	n.a.	300	1000
Nonylphenol	100	8300	330	n.a.

n.a.: not available

In the Llobregat river basin, the concentrations of atrazine and HCB in water are below the AA-EQS. However, in the case of NP, concentrations exceeding such threshold level were found. In 2005, 10 out of the 77 sites monitored exceeded the AA-EQS. However, this situation has improved in the last two years, in which less: non compliances have been registered (7 sites out of 71 in 2006 and 8 out of 28 in 2008). It is worth noting that in 2008 operational monitoring was focussed on problematic sites (hot spots), leaving the others aside. For PBDEs no data in water are available. Nevertheless, some information concerning PBDEs concentrations in sediments from the Llobregat River is shown in Annex I.

Table 4. PSs studied concentration in the Llobregat River (2004-2008).

Substance	**ng/L**		**ng/L**	
	min	**max**	**AA-EQS**	**MAC-EQS**
Atrazine	2	116	600	2000
penta-BDE	n.a.	n.a.	0.5	n.a.
DEHP	n.a.	n.a.	1300	n.a.
Hexachlorobenzene	0.1	3.2	10	50
Isoproturon	n.a.	n.a.	300	1000
Nonylphenol	100	700	330	n.a.

n.a.: not available

Similar concentration levels of atrazine and HCB were found in the Ter River in comparison with Llobregat River. Conversely, those of NP were lower (see Table 4), which is mainly explained due to lesser industrial activity. However, the concentrations exceeded the AA-EQS in one site in 2005 (n=62) and once again the same site in 2008 (n=24).

New data have been obtained from a waste water treatment plant study. Nonylphenol, HCB, DEHP, atrazine and isoproturon were analysed in 2 WWTP from the Ter river basin and 6 from Llobregat river basin. This study is in compliance with Regulation No 166/2006 (E-PRTR). In Annex II the concentration of different compounds analysed in the WWTP effluents are reported. In both rivers, the concentrations of atrazine, isoproturon and DEHP are low. For HCB in none sample the LOD was exceeded. Finally, NP was found at significant levels, between 0.33 and 13.6 μg/L. This can be related with a higher presence of industries in the Llobregat basin. However, the concentration of these compounds in WWTP effluent is not yet regulated, the E-PRTR only force to report it.

Meanwhile, for PBDEs, isoproturon, atrazine, HCB, DEHP and nonylphenol it is important the information provided by MODELKEY project that works with samples from Llobregat River.

In Annex III and Annex IV are summarized all the published data, including those obtained in the framework of MODELKEY as well as other scientific research.

4. Step 2. Inventory of sources

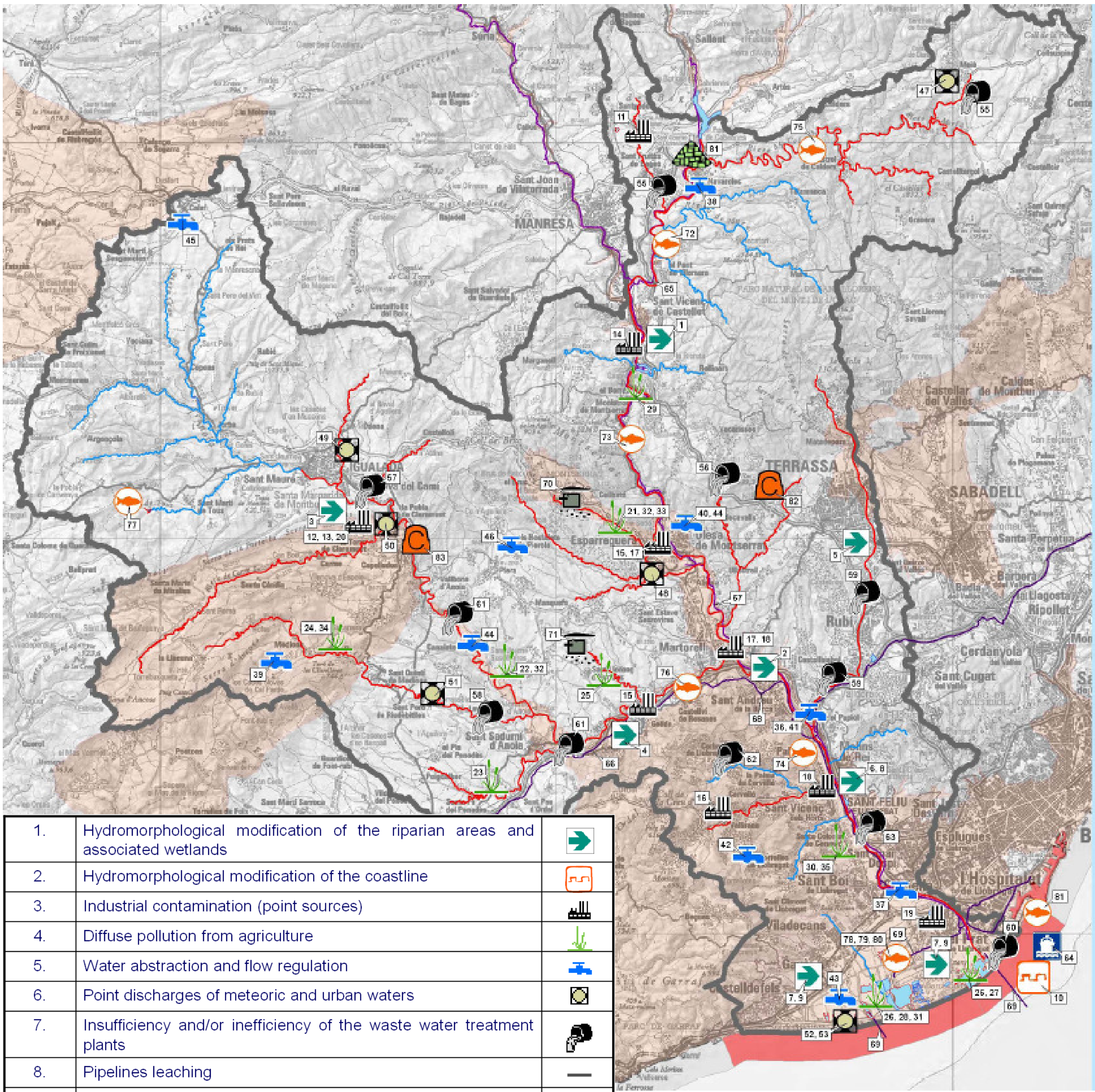
4.1. Point sources

The areas with industrial activity could affect the concentrations of the compounds under study in the river water. The possible sources of contamination are listed in Table 5. The pollution comes from agricultural activities, metallurgic, pulp mill, textile and tannery industries located in the studied area.

Table 5. Main sources of pollution.

<table>
<tr><th colspan="2">Llobregat</th><th colspan="2">Ter</th></tr>
<tr><th>Upper</th><th>Lower</th><th>Upper</th><th>Lower</th></tr>
<tr><td rowspan="6">Diffuse pollution from agriculture</td><td>Diffuse pollution from agriculture</td><td rowspan="6">Insufficiency and/or inefficiency of the waste water treatment plant</td><td>Diffuse pollution from agriculture</td></tr>
<tr><td>Industrial contamination (point sources)</td><td>Industrial contamination (point sources)</td></tr>
<tr><td>Insufficiency and/or inefficiency of the waste water treatment plant</td><td>Insufficiency and/or inefficiency of the waste water treatment plant</td></tr>
<tr><td>Point discharges of meteoric and urban waters</td><td>Point discharges of meteoric and urban waters</td></tr>
<tr><td>Contamination from leaching and storage of industrial residues</td><td rowspan="2">Contamination from leaching and storage of industrial residues</td></tr>
<tr><td>Scattered dwellings (urban waters)</td></tr>
</table>

For both rivers, the majority of problems are in the lower part (Figure 5 and 6), where are located cities and industrial areas. Thus, the point sources of HCB, NP, PBDEs and DEHP in Ter and Llobregat river basin area were identified. In the case of atrazine and isoproturon the sources are diffuse and attributable likely to agricultural activities.



1.	Hydromorphological modification of the riparian areas and associated wetlands	
2.	Hydromorphological modification of the coastline	
3.	Industrial contamination (point sources)	
4.	Diffuse pollution from agriculture	
5.	Water abstraction and flow regulation	
6.	Point discharges of meteoric and urban waters	
7.	Insufficiency and/or inefficiency of the waste water treatment plants	
8.	Pipelines leaching	
9.	Scattered dwellings (urban waters)	
10.	Invasive species	
11.	Contamination from leaching and storage of industrial residues	
12.	Diffuse pollution from livestock	

Figure 5. Possible sources of contamination in lower Llobregat River basin.

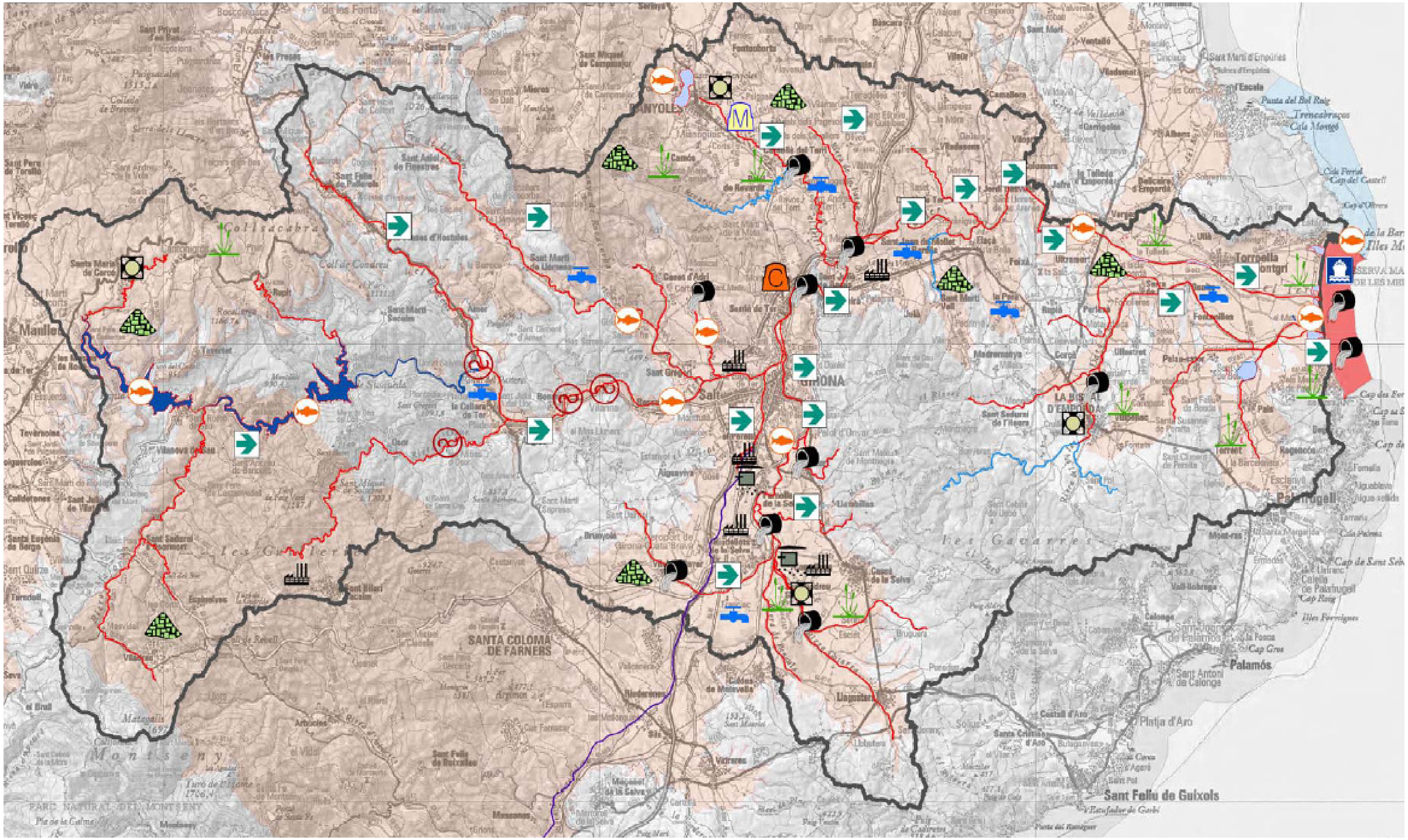


Figure 6. Possible sources of contamination in lower Ter River basin.

Furthermore, with the SCS (Source Category Split) from WP2 it is possible to obtain 40 sectors that could have an effect in the concentration for the six PSs considered in this case study. On the SCS are listed sectors that represent point and diffuse sources of these compounds (Annex V).

Another relevant characteristic is the distribution of population. The 92% of Catalonian inhabitants (7,364,078) are living in the internal basins (Figure 7), with the consequent necessity of drinking water supply and the corresponding generation of wastewater. In this way, the distribution of water uses in Catalonia is rather different depending on the basins concerned (Figure 8).

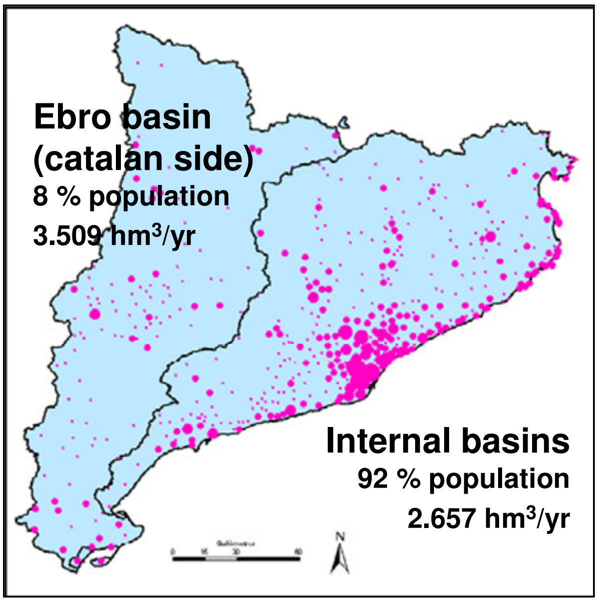


Figure 7. Distribution of population in Catalonia.

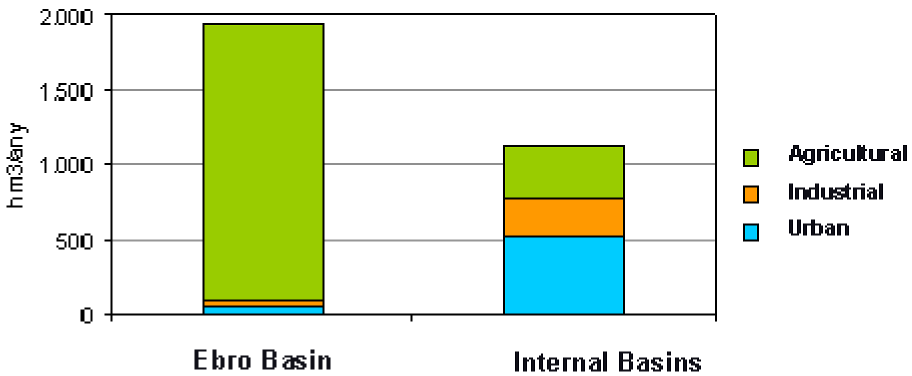


Figure 8. Water uses distribution in 2006.

4.2. Emissions factors

No information about emissions of PSs in Catalonia was available. It is important to be aware that in both rivers nearly all the municipal and industrial waste water are connected to public WWTP. For that reason, the data obtained for E-PRTR (2008) are so useful to estimate the quantity of compound discharged into the river.

Using the concentration values obtained and the average flow (2008) of the several WWTPs studied, the total emissions of the different compounds to the Ter and Llobregat Rivers were calculated. Thus in the Llobregat river (Table 6) the estimated emissions of NP, DEHP, atrazine and isoproturon show a major contribution of NP whereas, only DEHP was found in the WWTPs discharging into the Ter River (Table 7).

Table 6. Emission of PSs from WWTPs to Llobregat River.

WWTP	Kg/year				
	NP	HCB	DEHP	Atrazine	Isoproturon
1	5	-	-	-	0.3
2	-	-	-	0.013	-
3	573	-	3	6.17	1.1
4	10	-	0.35	0.02	0.2
5	242	-	5.14	0.09	-
6	6	-	2.41	0.08	1.5
∑	831	-	10.9	6.36	2.8

Nº eq-inhabitants: 2,322,155

Table 7. Emission of PSs from WWTPs to Ter River.

WWTP	Kg/year				
	NP	HCB	DEHP	Atrazine	Isoproturon
1	-	-	-	-	-
2	-	-	19.6	-	-
∑	-	-	19.6	-	-

Nº eq-inhabitants: 389,485

5. Step 3. Definition of baseline scenario

5.1. Is there any reason to presume that the future water quality will be different from the current status?

To answer this question, is important to keep on mind the fact that the PSs under study are or will be banned in the near future, so the main sources of pollution are likely to be eliminated or now exists plans to eliminate before 2015. On the other hand, the future water quality could be different due to:

- **Population growth and concentration.** Despite water saving policies, increases in population will lead to an increase in demand, in particular for urban supply. It is estimated that by 2025 the demand from urban networks, witch currently stands at 750 hm^3/year, will have risen by around 160 hm^3/year (110 hm^3/year in the Ter-Llobregat system). Catalan population currently stands at 7 million inhabitants, and could be close to 8.5 million by 2025.
- **Extreme events like floods and droughts.** Catalan rivers are subjected to sequential seasonal events showing high flow regime variation and extreme events like sudden floods and severe droughts, affecting the water supply. Furthermore, according to the changing climate scenarios foreseen by the Intergovernmental Panel on Climate Change (IPCC) for the Mediterranean area, the frequency and intensity of such extreme events will tend to increase in the medium future. For that reason, the authority should be prepared for different problems, like drinking water failing of guarantee, vulnerability of resources and lack of system flexibility or water quality problems. In order to solve these difficulties, the water authority developed some future action plans that are summarised in Table 8.

Table 8. Drinking water resource (hm^3) allocation in year 2005 and 2025.

Resource allocation	2005	2025
Ter	190	120
Llobregat	150	140
Groundwater	30	40
Non conventional resources (desalinisation, reuse, etc.)	-	160

- **Changes in land use – climatic change.**
- **Diffuse and point pollution.**
- **Hydromorphological alterations**
- **Ecosystem alterations.**

All these issues could cause problems in the river basin: increase in the water demand; water scarcity; loss of water chemical quality and loss of ecological quality. However, regarding the studied compounds, the future water quality will be better than now mainly because of the measures to be taken in fulfilment of the WFD. An example is the *Wastewater Treatment Plan of Catalonia* that has achieved a notable improvement in the chemical quality of Catalan river water with 337 WWTP in operation and 174 under construction.

5.2. Environmental Fate Analysis

For a better understanding of the system, an environmental quantitative fate analysis was performed with QWASI program using the data obtained from E-PRTR monitoring. The results obtained are summarized in Table 9. This information allows to compare the behaviour of the same compound in both rivers, as well as the behaviour of different compounds in the same river. In the case of PBDEs, the estimation was performed assuming a discharge into water of 100 Kg/year for penta-BDE and deca-BDE. However, the obtained data does not reflect the real environmental behaviour.

Tabla 9. Main results obtained from an environmental fate analysis.

	Ter	**Llobregat**			
	DEHP	**NP**	**DEHP**	**Atrazine**	**Isoproturon**
Direct discharges into water from WWTP (Kg/year)	19.6	831	10.9	6.4	2.8
Evaporation from water (Kg/year)	$2.3*10^{-4}$	140	$1.5*10^{-4}$	$5.5*10^{-5}$	$1.86*10^{-5}$
Concentration in water (ng/L)	18.36	936	11.82	9.04	3.72
Reaction into water (Kg/year)	0.78	13.25	0.5022	0.0271	0.1884
Kg/year to sediment	3.31	30.58	2.13	0.1921	0.0786
Residence time in water (d)	2.87	3.42	3.32	4.23	3.97
Residence time in sediment (d)	17.94	303	17.93	23.6	12.9

Table 9 showed the concentrations in water of the compounds studied. Only NP does not fulfil the EQS proposed by WFD. Taking into consideration that the EQS for NP is 300 ng/L, and the relation between concentration and emission, the maximum discharge of NP from the WWTP should be 266 Kg/year. The possible sources of NP are the industries located in the river basin. Therefore, this is consistent with the results found for the two rivers, which show in the Llobregat a greater exceedance than in the Ter River.

In the future, taking into account the present and projected measures, it is expected to fulfil the EQS of NP in all areas. The main measure to improve the water chemical quality is the *Urban Wastewater Treatment Program*. There are 335 WWTP in service in Catalonia (2008) and until 2014, 998 new WWTP forecast. On the other hand, the measures to increase the supply guarantee are:

- Municipal supply master plans
- Urban water supply saving programme
- Programme for efficiency in the use and improvement of the quality of groundwater bodies in the lower Ter and lower Llobregat.
- Plan for efficient water use in agricultural irrigation
- Catalan Water Reuse Program
- Sector Plan for Water Supply in Catalonia
- Lines of support for local supply

Some of these measures are now developed; the others are in curse but the resources had been approved (Table 10).

Table 10. Measures to increase the water supply guarantee in internal basin.

Action	Total Amount (€M including VAT)	Resources (hm^3/year)	Estimated entry into service
Barcelona metropolitan area desalinination plant	238	60	2009
Enlargement and improvement of treatment at the Abrera drinking-water plant	66	20	2008
Extension of the Abrera-Fontsanta pipe to El Prat de Llobregat	30	System improvements	2008
Addition to the connection between the Abrera and Cardedeu WWTPs: Fontsanta-Trinitat section	152	System improvements	2010
Reinforcement of the supply from the Costa Brava Centre	56	System improvements	2009
Additional water treatment actions in Martorell, Rubi and Igualada	29	5	2011-2012
Additional water treatment actions in Sant Feliu, Gavà and El Prat de Llobregat	51	20	2009-2010
Supply from La Llosa del Cavall	46	System improvements	2010
Division of the Cardedeu-Trinitat artery	32	System improvements	2009
Regulations ponds for the Sant Joan Despí drinking-water plants	35	10	2010
Replenish ponds at the El Baix Llobregat aquifer	10	10	2010

Decontamination of the Besòs aquifer	14	10	2011-2015
Water saving and sustainable management programme. Improvement of the waterproofing of the supply networks	31	5	2011-2015
Hydrological-environmental restoration of the saline residue from the river Llobregat to improve the quality of the water	46	Quality improvements	2011-2015
Hydro-morphological recovery of the rivers Cardener, Llobregat and Ter	28	Quality improvements	2011-2015
Interconnection of the El Maresme, North and ATLL supply networks	47	System improvements	2008-2009
Extension of the Tordera desalination plant and new catchment	49	(10+) 10	2009-2010
Connection of Tordera desalination plant -Ter drinking- water plant	100	System improvements	2009-2010
Southern coast desalination plant	280	20 + 20 + 20	2010-2012
Reuse of use of local resources in El Camp de Tarragona and the CAT	207	20	2010-2011
New desalination plant at the Tordera	150	30 + 30	2012
TOTAL	**1,697**	**300**	

6. Step 4. Identification of possible measures

Actually in Ter and Llobregat rivers there is a good status for the studied PSs. Only in the case of NP, some measures are needed (Table 11). However, in the last years a progressive decrease in the levels of nonylphenol found in the Llobregat and Ter Rivers has been observed. Therefore, upon application of the above measures it is expected the compliance with the AA-EQS required by the WFD.

Table 11. Possible measures of NP applicable to Ter/Llobregat river basin.

Source	Measures
Industrial processes Leather processing Detergent and cleaning agents Manufacturing of paints Textile processing	Substitution of NPE by alcohol ethoxylates
Waste disposal/waste generation Waste water treatment plants Municipal sewage sludge application Paper recycling	Improvement of WWTP: a. Use of new technologies (biomembranes, Reverse Osmosis, Advanced Oxidation Treatments) b. Activated coal adsorption filters

7. Conclusions.

A decision support system (DSS) was developed by WP4 to support water authorities to make plans and decisions for the control of priority substances (PSs) in fulfilment of the Water Framework Directive (WFD; 2000/60/EC).

This tool contains seven sequential steps and was applied in a case study from south of Europe: Ter and Llobregat rivers (Spain). The selected PSs were: Atrazine, [Di(2-ethylexyl)-phtalate] (DEHP), Hexachlorobenzene (HCB), Isoproturon, Nonylphenol (NP) and Polybrominated diphenylethers (PBDEs).

Enough data was obtained to carry on this study, mainly from the quality control network of Catalan Water Agency (ACA) that was implemented in order to achieve the WFD. Therefore, is important to continue with the monitoring of PSs and search for new potential substances. Useful information for the progress of the study was generated by WP2 and WP3, making possible to harmonize and organize the results and experiences with the other case studies.

The majority of compounds have a lower concentration than the maximum allowable concentration (MAC) from Environmental Quality Standards (EQS), just in the case of NP is possible to see an excess in 2005. It is important to note that most of the nonylphenol emissions to water are from industrial sources that are discharged to surface water after being treated in a waste water treatment plant (WWTP). Thus, the *Wastewater Treatment Plan of Catalonia* has achieved a notable improvement in the Catalonia's river water with 337 treatments plants in operation. On the other hand, as a result of the unsuitable or accidental release of polluted waste water with not treatment or uncorrected treatment, localised impacts could be found. For this reason, important information was obtained in a study performed in agreement of Regulation No 166/2006 (E-PRTR) that analysed PSs in the effluent of the most important WWTP from rivers Ter and Llobregat.

Since the enforcement of the EU Directive 2000/60/EC, most of the uses of PSs in study have been phased out in all EU member states. However, some compounds could be already been used due to its usefulness and low cost; this is the case of atrazine.

It is important to note that Llobregat and Ter river basin are dominated by a Mediterranean climate, typically has an irregular rainfall pattern. Therefore, this system is highly vulnerable in terms of guaranteeing supply as the quantity of water available is limited.

Future chemical status of both basins should be better due to the agreement of the actual legislated levels of WFD compounds. However, other problems like drought and increasing of population could affect the water quality. Finally, another task to be in account is the analysis of sediments and biota (both matrix are not legislated) and not legislated compounds, like pharmaceuticals, abuse drugs, estrogens and other pesticides.

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8. Annexes

8.1. Annex I. BFRs concentration levels (expressed in ng/g dry mass) in Llobregat and Anoia River sediments (Guerra et al., 2009).

	LL1			LL2		LL3			LL4			A1		A2			A3		
	C1	**C2**	**C3**	**C2**	**C3**	**C1**	**C2**	**C3**	**C1**	**C2**	**C3**	**C1**	**C2**	**C1**	**C2**	**C3**	**C1**	**C2**	**C3**
BDE-49+71	nq	nq	nd	4.9	nd	nq	0.9	nq	5.3	nd	nd	nd	1.0	0.3	nq	nq	nd	4.7	nq
BDE-47	nq	nq	nq	1.4	nq	nq	nq	nq	2.6	nq	nd	nd	nq	3.2	nq	nq	nd	8.7	nq
BDE-100	nq	nq	nq	nq	nd	nq	nd	nq	1.0	nq	nd	nd	nd	nd	nq	nq	nd	nd	nq
BDE-99	nd	nq	nq	nq	nq	nq	nq	nq	10	nq	nd	nd	nq	nd	nq	nq	nd	3.3	nq
BDE-153	nd	10	17	nq	nd	4.4	nq	nd	nq	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-201	nd	nd	nd	nd	nd	nd	nd	3.3	nd	nd	nd	nd	nd	nd	nd	nd	4.2	nd	nd
BDE-204+197	nd	nd	nd	4.0	nd	nd	nd	12	nd	nd	nd	nd	nd	nd	4.5	nd	5.5	nd	nd
BDE-203	nd	nd	nd	2.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-196	nd	nd	nd	3.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-208	4.6	8.0	6.3	9.5	7.6	5.8	6.4	12	9.3	7.9	5.2	6.5	6.4	6.3	7.6	6.3	8.8	6.4	4.6
BDE-207	4.5	3.8	6.1	13	8.6	6.4	7.4	12	12	9.0	5.9	7.4	6.9	6.8	8.2	7	11	6.9	4.5
BDE-206	5.0	nq	8.1	15	11	6.1	9.7	20	11	11	12	8.4	9	10	8.5	11	24	10	7.7
BDE-209	7.8	9.9	7.7	82	13	7.5	5.2	29	21	29	56	3.2	4.1	19	17	11	57	36	11
Total PBDEs	22	32	45	136	40	30	30	89	73	57	79	26	27	46	46	35	111	76	28
Emerging BFRs																			
PBEB	9.0	7.7	nq	4.7	nq	6.1	8.2	nd	5.5	9.1	nd	6.4	9.0	9.6	3.1	nd	8.3	6.7	nd
hexaBBz	nq	nd	nd	2.2	nd	nq	nd	nq	2.4	nd	nd	nq	nd	nd	nq	nq	nd	0.4	nq
DeBDethane	8.6	4.8	12	23	12	9.1	13	10	9.9	11	24	9.1	15	15	15	13	20	11	22

LL: Llobregat River; A: Anoia River; C1: First sampling campaign (June 2005); C2: Second sampling campaign (October 2005); C3: Third sampling campaign (June 2006); nd: below LOD; nq: below LOQ.

8.2. Annex II. PSs concentration in WWTP effluent from Llobregat and Ter River (E-PRTR, 2008).

WWTP		Atrazine (µg/L)	Isoproturon (µg/L)	Nonylphenol (µg/L)	HCB (µg/L)	DEHP (µg/L)
Llobregat	1	< LOD.	0.02	0.33	< LOD.	< LOD.
	2	0.01	< LOD.	< LOD.	< LOD.	< LOD.
	3	0.06	0.01	5.8	< LOD.	0.03
	4	0.002	< LOD.	1.2	< LOD.	0.04
	5	0.005	0.01	13.6	< LOD.	0.29
	6	0.005	< LOD.	0.35	< LOD.	0.15
Ter	1	< LOD.	< LOD.	< LOD.	< LOD.	2.8
	2	0.003	< LOD.	< LOD.	< LOD.	< LOD.

LOD: Limit of detection (µg/L); Atrazine (LOD): 0.004; Isoproturon (LOD): 0.008; NP (LOD): 0.15; HCB (LOD): 0.005; DEHP (LOD): 0.0001.

8.3. Annex III. Concentration of PSs in influent and effluent water and sludge from WWTP located in Llobregat and Ter rivers.

Compound	LLOBREGAT			TER	
	WWTP influent (ng/mL)	**WWTP effluent (ng/mL)**	**Sludge (µg/g)**	**WWTP influent (ng/mL)**	**WWTP effluent (ng/mL)**
Atrazine	-	-	-	-	-
Di(2-ethylhexyl)-phthalate (DEHP)	-	-	2.0-512[a,b]	-	-
Isoproturon	-	-	-	-	-
Nonylphenol	0.5 – 44800[c-f]	< 0.1-3000[c-f]	85-172[f]	<0.07-17.5[g]	0.33-2.07[g]
Polybrominated diphenyl ether (PBDE)	-	-	-	-	-

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8.4. Annex IV. Concentration of PSs water. sediment and biota from Llobregat and Ter rivers**.**

Compound	**LLOBREGAT**			**TER**
	Water (ng/mL)	**Sediment (ng/g dw)**	**Biota (ng/g lw)**	**Water (ng/mL)**
Atrazine	0.005-0.463[a-c]	-	-	-
Di(2-ethylhexyl)-phthalate (DEHP)	-	-	-	-
Isoproturon	0.0005-0.503[b,c]	-	-	-
Nonylphenol	<0.15 – 398[d-i]	<50-630[f]	450-5400[j]	<0.07-1.32[l]
Polybrominated diphenyl ether (PBDE)	-	2.47-9.75[k]	30.1-744[k]	-

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8.5. Annex V. Sectors and sources potentially important in Ter and Llobregat river basin.

SCS code	Source	NACE	Substances of concern
1	**Combustion of fuels**		
1.4	Combustion of coal in residential units		HCB
1.7	Combustion of wood		HCB
2	**Industrial processes**		
2.21	Manufacturing of polymers		DEHP
2.24	Manufacturing of paints	24.30	NP
2.27	Plastics processing	25.20	PBDES
2.28	Textile processing	17.00	NP, PBDES
2.31	Leather processing	19.00	NP
3	**Waste disposal/waste generation**		
3.1	Incineration of wastes		HCB, DEHP, PBDE
3.3	Waste water treatment plants		HCB, DEHP, NP, PBDE
3.4	Land-filling of various food and agriculture wastes		HCB, PBDE
3.5	Land-filling of urban refuge and commercial products		HCB, DEHP, NP, PBDE
3.6	Municipal sewage sludge application		DEHP, NP, PBDE, atrazine, isoproturon
3.8	Demolition of preserved wood, other dismantling and crushing activities		DEHP
3.9	Car shredder		DEHP, NP
3.10	Paper recycling		DEHP
3.11	uncontrolled burning of wastes, electronic goods, agricultural wastes		PBDE
3.12	Public laundries		PBDE
3.13	Collection and treatment of wastes	90.02	PBDE
4	**Transport**		
4.2	Water transport	61.00	DEHP
4.3	Air transport	62.00	NP
5	**Agriculture activities**		
5.1	Animal husbandry and agriculture	1.40	NP

5.2	Field application as fungicide		HCB
5.3	Field application as pesticides or impurities in pesticides		HCB, NP, PBDE, atrazine, isoproturon
6	**Uses of chemicals**		
6.3	Use of solvents	74.70	HCB, NP
6.4	Wood protection products		HCB
6.7	Paint and stain use		NP
6.8	Plasticizer use		DEHP
6.9	Industrial processing of non-polymer		DEHP
6.1	Polymer-indoor use		DEHP
6.11	Polymer-outdoor use		DEHP
6.12	Non-polymer indoor use		DEHP
6.13	Non-polymer outdoor use		DEHP
6.14	Flexible polyurethane foam use		PBDE
6.15	Solid polyurethane foam use		PBDE
6.16	Electrical appliances		PBDE
6.17	Emulsion polymerisation		NP
6.19	Treatment and coating of metals	28.51	NP
6.2	Urban storm water		DEHP, NP, PBDE, atrazine
7	**Other sources**		
7.1	Atmospheric deposition to water		HCB, PBDE, atrazine, isoproturon
7.2	Atmospheric deposition to land		HCB, PBDE, atrazine, isoproturon
7.3	Sediment re-suspension		PBDE
7.5	Volatilization from soils and leaves		atrazine, isoproturon
7.6	Wind erosion		atrazine, isoproturon
7.7	Surface runoff		atrazine, isoproturon