MONITORING PRIORITY POLLUTANTS AND EMERGING CONTAMINANTS IN THE WATER-SEDIMENT SYSTEM OF THE EBRO RIVER BASIN (AQUATERRA PROJECT)

DAMIA BARCELO

Alicia Navarro, Alain Hildebrandt, Silvia Lacorte, Meritxell Gros, Miren Lopez de Alda, Marina Kuster, Mira Petrovic, Ethel Eljarrat, Carlos Barata, Demetrio Raldua

IIQAB-CSIC, BARCELONA, SPAIN

dbcqam@cid.csic.es

Agenda

- **Aquaterra project - objectives**
- **Monitoring at Ebro river basin**
  - **Surveillance monitoring**
    - Priority pollutants
  - **Operational monitoring**
    - Pharmaceuticals in river and waste water
  - **Investigative monitoring**
    - Brominated flame retardants at two risk zones
    - Distribution and biological impact of dioxin-like compounds in risk zones
    - Polar pesticides in the Delta of Ebro
- **Management of the monitoring data**
- **Conclusions**

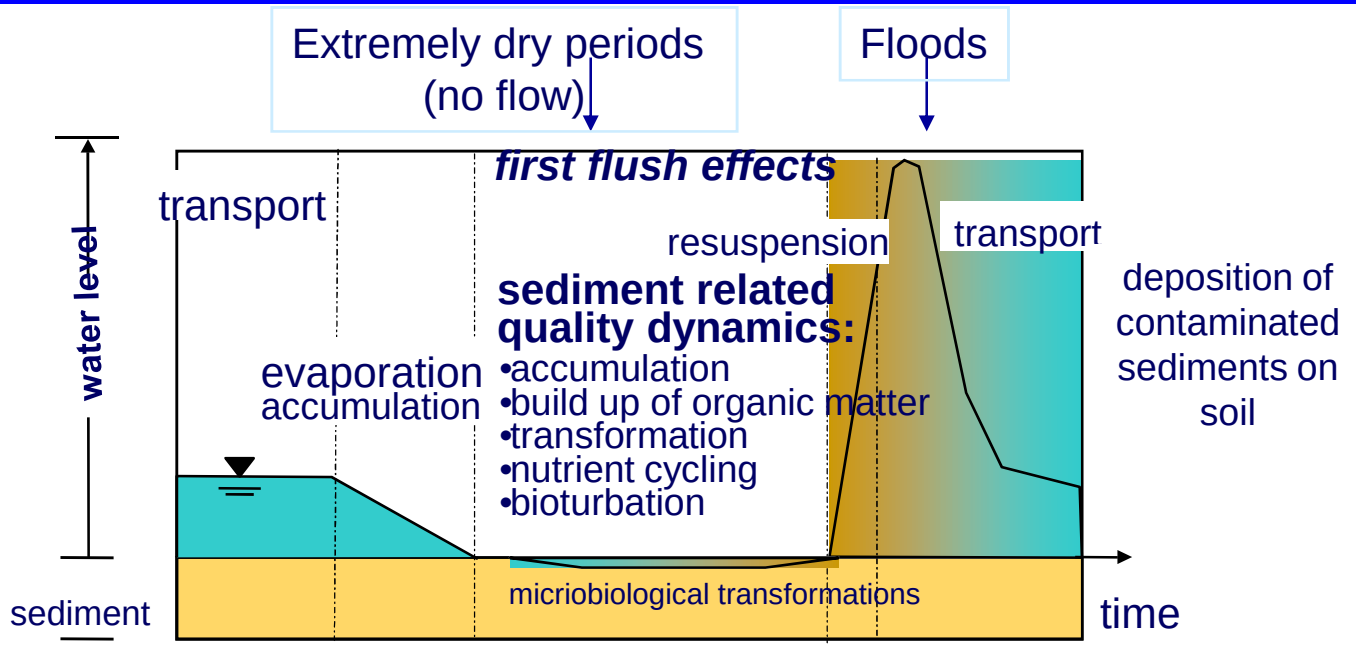
AQUATERRA Project

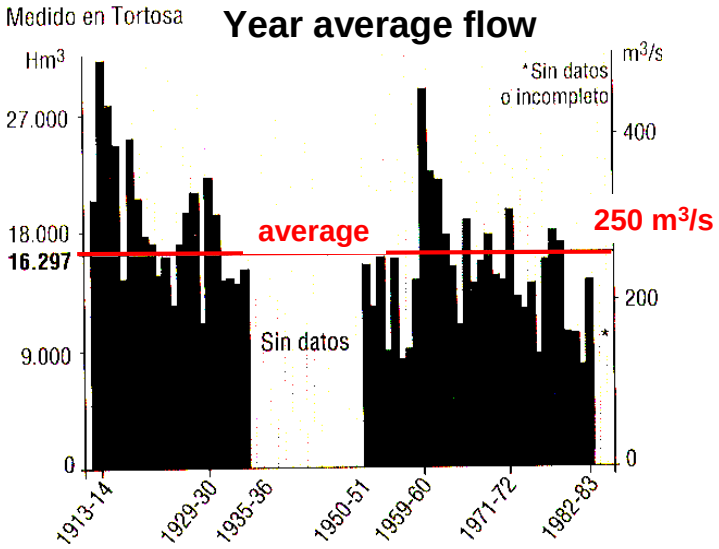
MONITORING SOIL- WATER –SEDIMENT INTERACTIONS AT **EBRO RIVER BASIN**

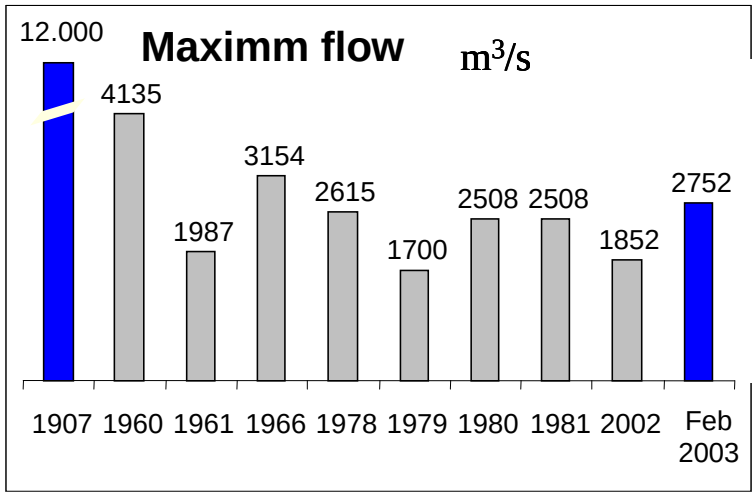
Objectives

- impact of changing hydrological and seasonal conditions and mega-loadings during extreme hydrological events (resuspension of sediments, deposition onto soil)
- groundwater quality/quantity and the functioning of the soil as filter/buffer/transform/storage medium
- groundwater quality trends in relation to an extensive agricultural activity
- air-soil-groundwater transport of organic pollutants
- behaviour and fate of pollutants; bioavailability; speciation

EBRO: Typical Mediterranean river- Extreme hydrological conditions





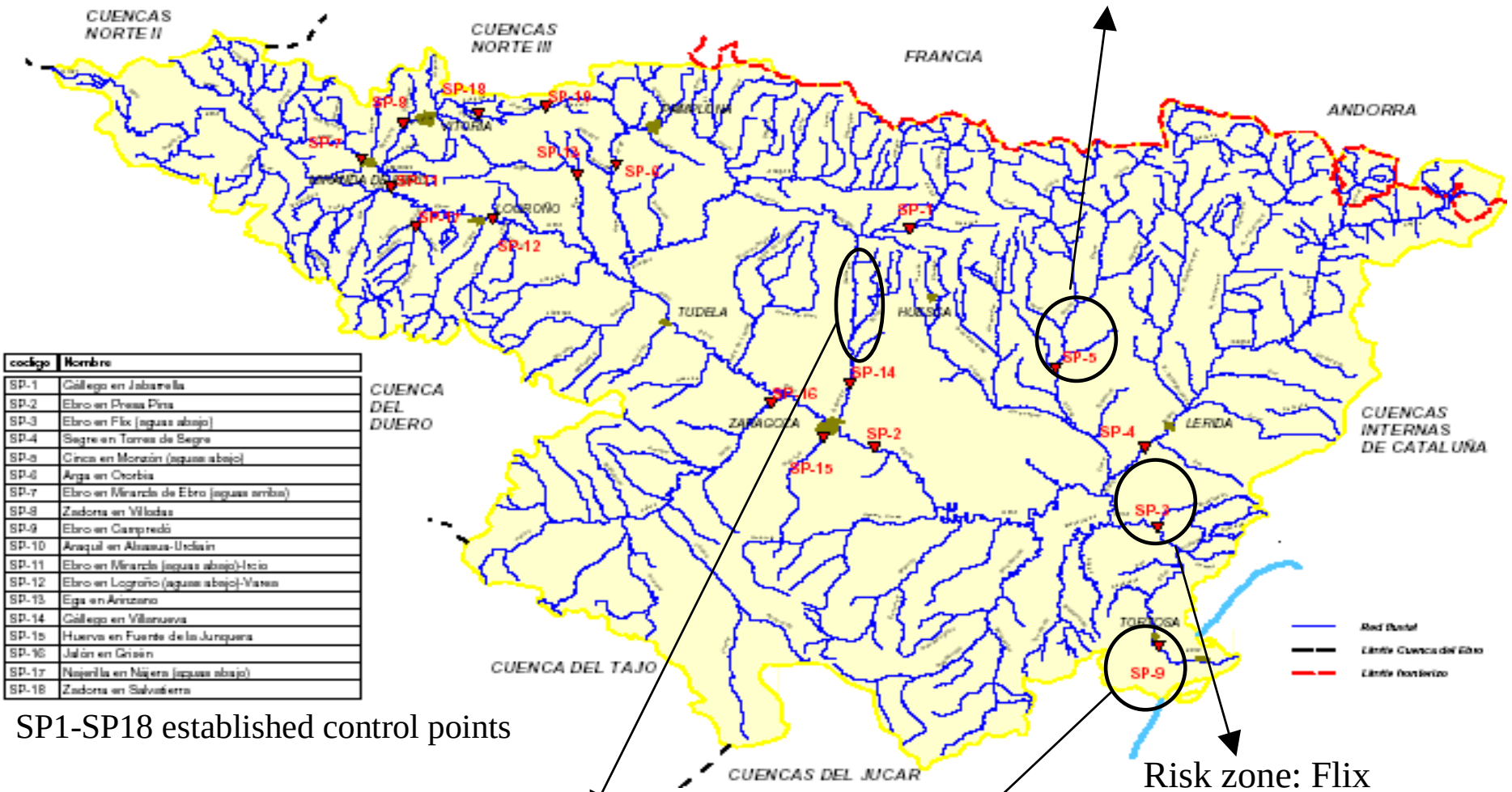


AQUATERRA Project

1. **Surveillance monitoring** (SM) will provide assessment of long-term changes natural or anthropogenic, adequate preparation of future monitoring programs [priority pollutants Directives 2006/11/CE (previous 76/464/CEE) and 2455/2001/EC]
   - *24 monitoring stations along the Ebro (surface water, sediment);*
   - *8 sampling points for ground water and soil*
2. **Operational monitoring** (OM) will classify status of water bodies identified as being at risk of failing environmental conditions (**emerging contaminants**)
   - *9 monitoring stations along the Ebro (surface water and sediment)*
   - *6 wastewater treatment plants*
3. **Investigative monitoring (IM)** , when SM shows that environmental objectives are not met or to assess the impact of accidental pollution events (priority pollutants + **emerging contaminants**)
   - *19 sampling points in three polluted(Industry/Agricultural) zones: MONZÓN, FLIX and EBRO DELTA*

Surveillance monitoring + Specific case study areas

Risk zone: Cinca River



codigo	Nombre
SP-1	Gállego en Jabarrella
SP-2	Ebro en Presa Pina
SP-3	Ebro en Flix (aguas abajo)
SP-4	Segre en Torres de Segre
SP-5	Cinca en Monzón (aguas abajo)
SP-6	Arga en Ororbia
SP-7	Ebro en Miranda de Ebro (aguas arriba)
SP-8	Zadorra en Villodas
SP-9	Ebro en Campredó
SP-10	Araquil en Alsasua-Urdiain
SP-11	Ebro en Miranda (aguas abajo)-Inicio
SP-12	Ebro en Logroño (aguas abajo)-Varea
SP-13	Ega en Arinzano
SP-14	Gállego en Villanueva
SP-15	Huerva en Fuente de la Junquera
SP-16	Jalón en Grisén
SP-17	Najerilla en Nájera (aguas abajo)
SP-18	Zadorra en Salvatierra

SP1-SP18 established control points

Gallego catchment

Risk zone: Estuary

Risk zone: Flix

Surveillance monitoring
Priority compounds (Directives 2006/11/CE, 2455/2001/EC)

Pesticides

Alachlor
Atrazine
Atrazine-desethyl
Azinphoos-ethyl
Bromophos-ethyl
Bromophos-methyl
Chlorfenvinphos
Chlorpyriphos
Diazinon
Dichlofenthion
Dimethoate
Ethion
Fenchlorphos
Fenitrothion
Malathion
Metolachlor
Molinate
Omethoate
Parathion-ethyl
Parathion-methyl
Propanil
Propazine
Simazine
Terbuthylazine
Terbutryn
Tributylphosphate
Trifluralin

Aldrin
Dieldrin
Isodrin
Endrin
Endrin aldehyde
2,4-DDD
4,4-DDD
2,4-DDE
4,4-DDE
2,4-DDT
4,4-DDT
alpha-endosulfan
beta-endosulfan
endosulfan-sulfate
alpha-HCH
beta-HCH
delta-HCH
gamma-HCH
Heptachlor
Heptachlor-exo-epoxide
Heptachlor-endo-epoxide
Hexachlorobenzene
Pentachlorobenzene

PAHs & NPs:

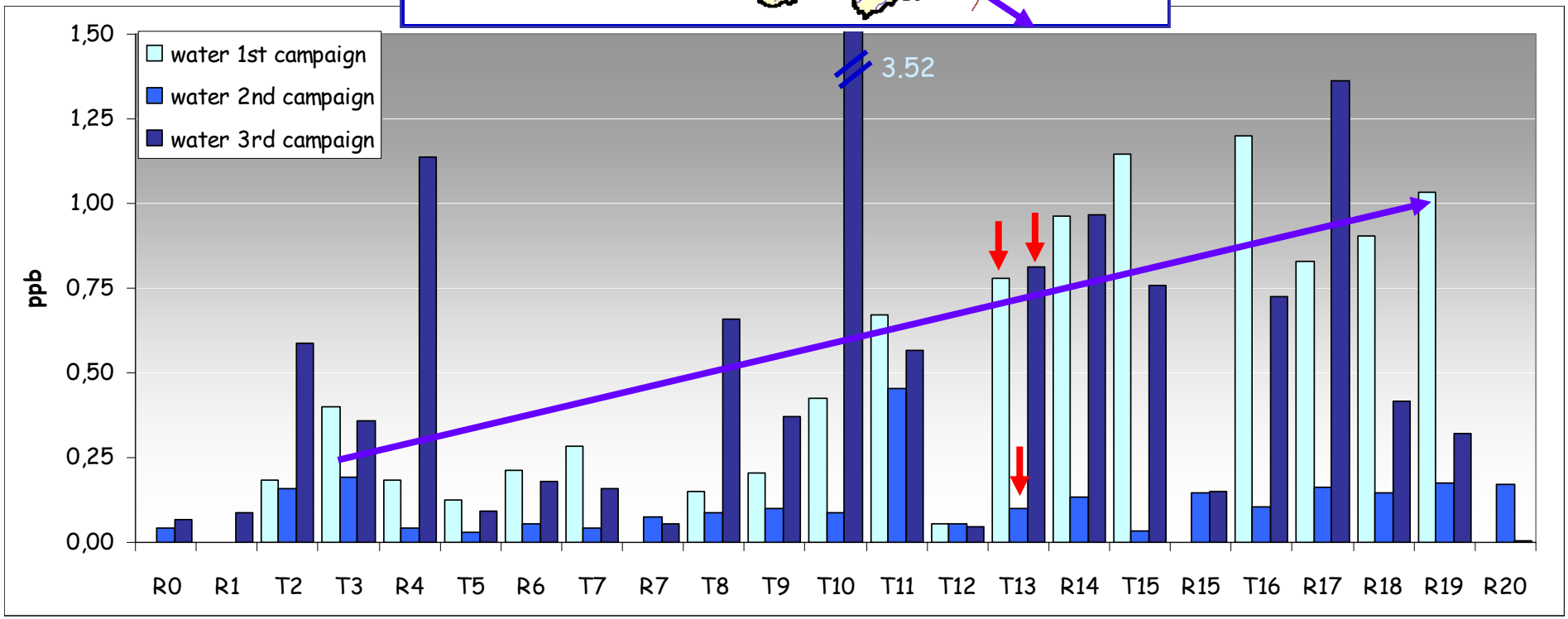
Acenaphthene
Acenaphtylene
Anthracene
Benzo(a) anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k) fluoranthene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphtalene
Phenanthrene
Pyrene

and

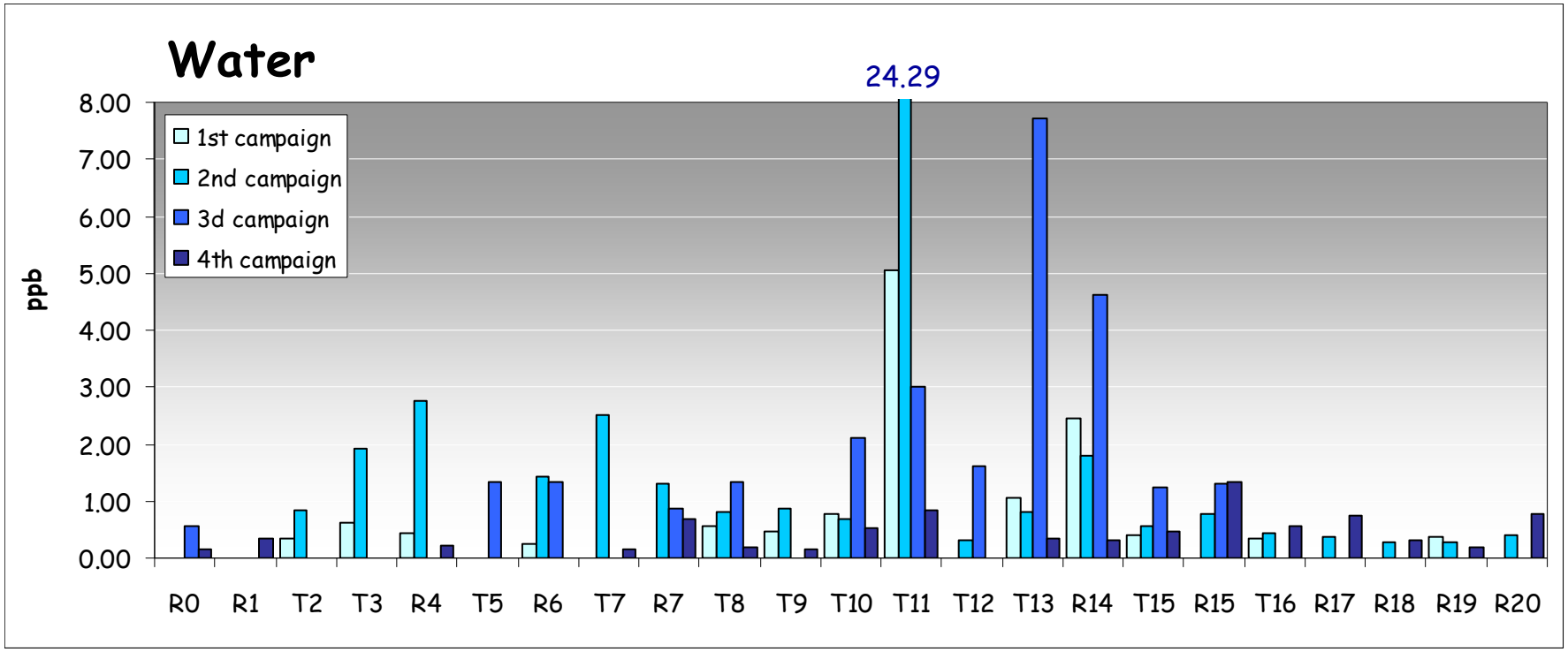
Octylphenol
Nonylphenol
Bisphenol A

69 compounds

Surveillance monitoring - Polar pesticides in river water

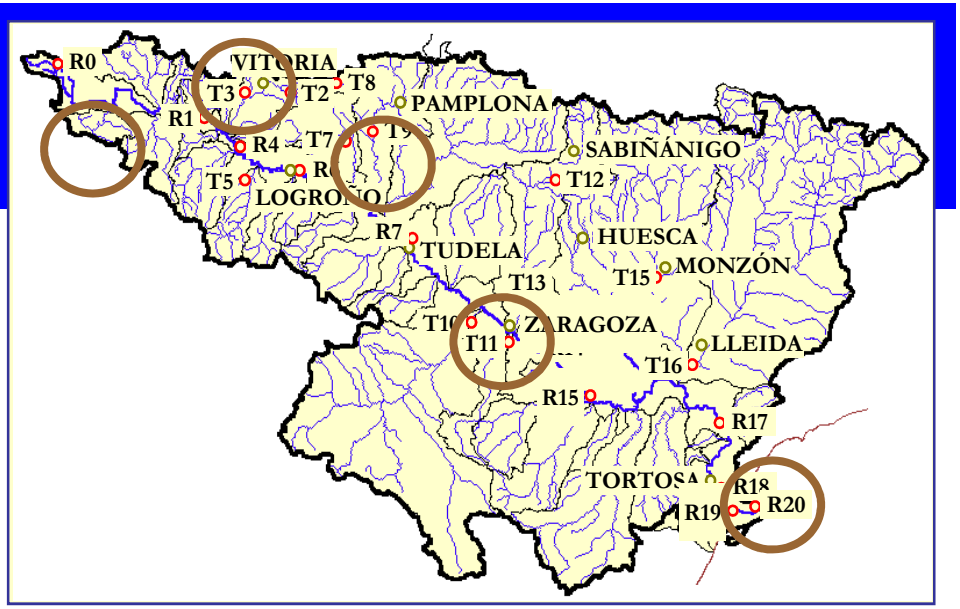


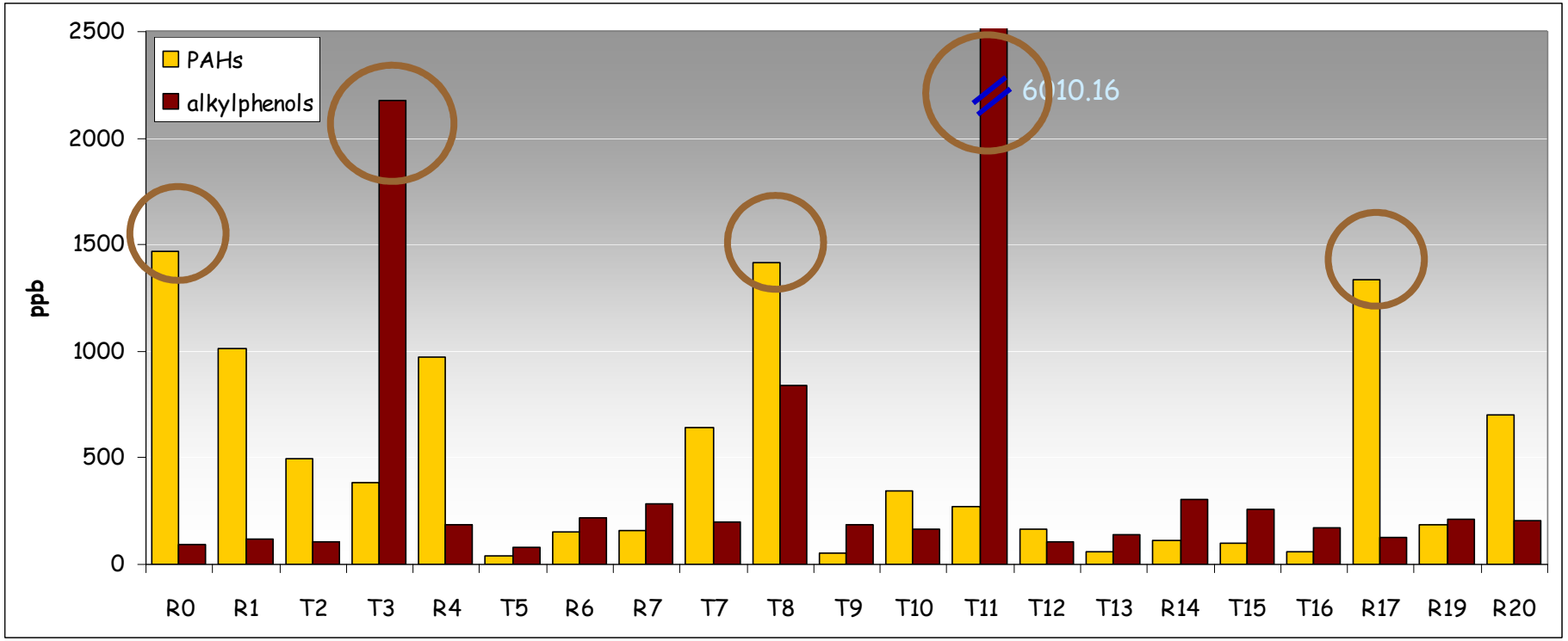
Surveillance monitoring – Nonylphenol in river water



- Nonylphenol appears in water from all the sampling campaigns and in all the sampling site in more or less concentration
- It appears at high concentrations in some sampling sites

Surveillance monitoring
Sediments





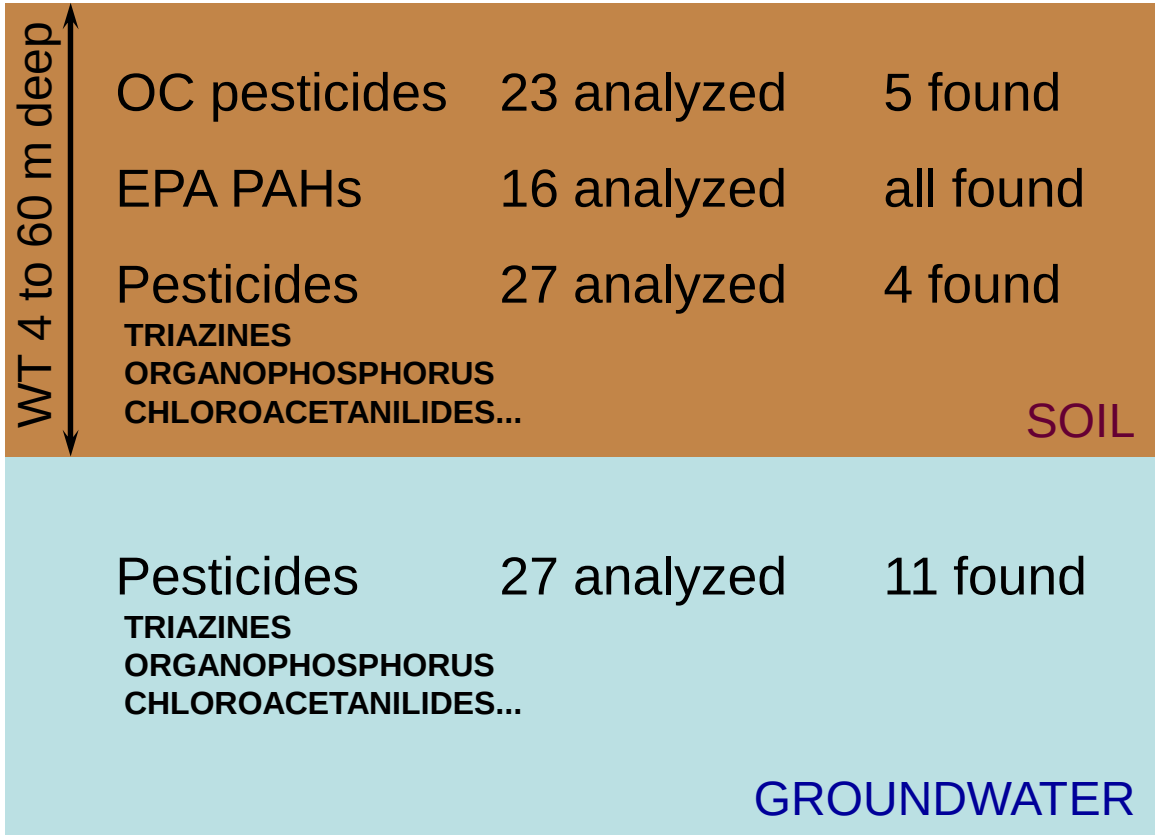
Surveillance monitoring: Groundwater

OBJECTIVES

To study the occurrence of multi class pesticides and PAHs in agricultural soils and evaluate the leaching potential through a 3 year monitoring period (2 sampling campaigns per year).

To estimate temporal and geographical trends.

TARGET COMPOUNDS AND MATRIX



Sample: 0-10 cm

TOC 0.6 - 3.9%

Sample: 1 m under WT

pH 5.52 - 7.81

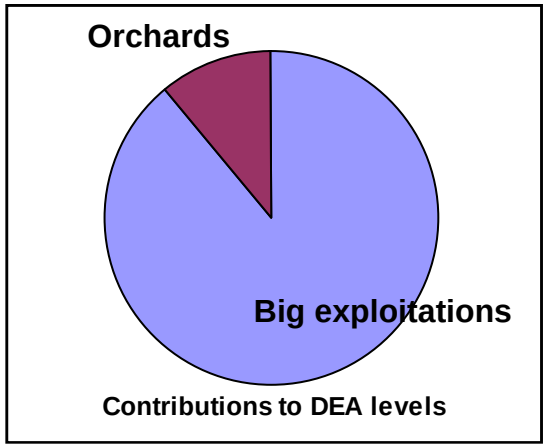
Cond. 681 - 5658 µS/cm

Temp. 12.21 - 24.20 ºC

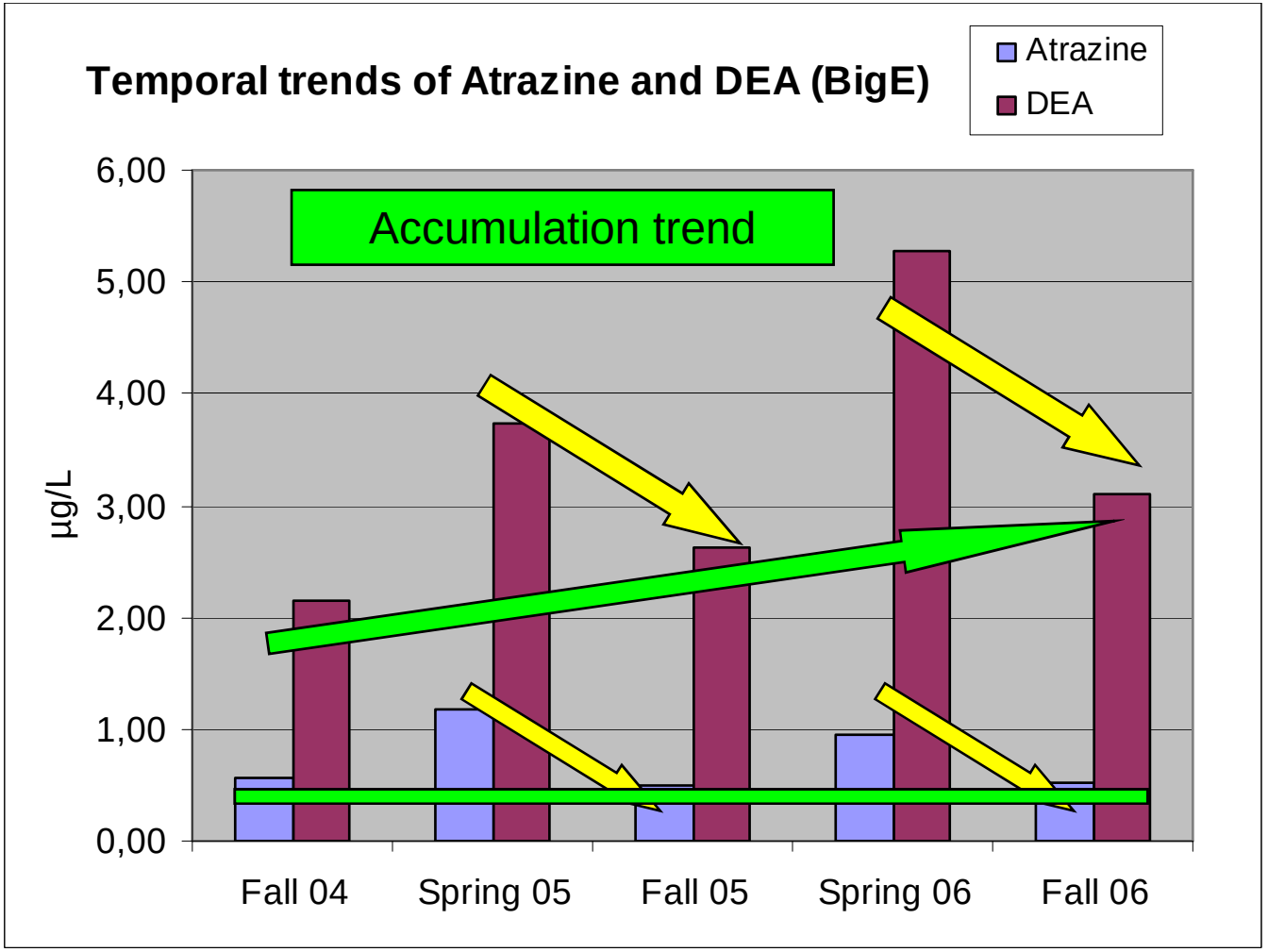
LEVELS IN THE EBRO RIVER BASIN

Groundwater samples: summarized results for pesticides

Compound	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Detection over the quantification limit (95 water samples)
Tributylphosphate	0,01	0,73	0,08	69%
Desethyl atrazine	0,01	1,87	0,31	69%
Simazine	0,01	0,11	0,04	60%
Atrazine	0,01	0,37	0,08	58%
Terbuthylazina	0,01	0,35	0,08	37%
Propanil	0,01	0,02	0,02	20%
Alachlor	0,02	0,51	0,13	9%
Azinphos-ethyl	0,03	0,57	0,22	3%
Metolachlor	0,01	5,37	1,82	3%
Diazinon	0,02	0,06	0,04	2%
Fenitrotion	0,15	0,15	0,15	1%
Terbutryn	0,07	0,07	0,07	1%
gamma-HCH	0,46	0,46	0,46	1%



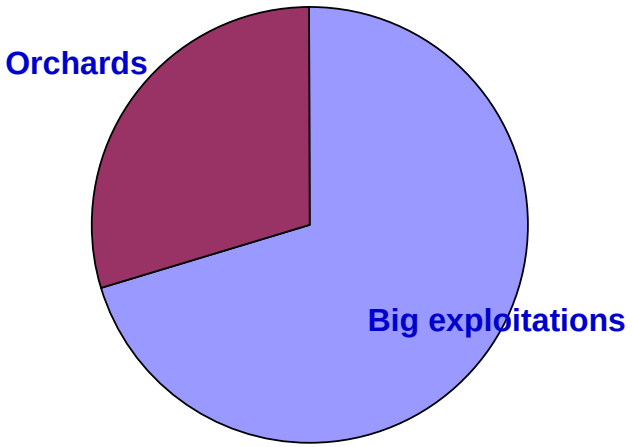
LEVELS IN THE EBRO RIVER BASIN



LEVELS IN THE EBRO RIVER BASIN

Soil samples: summarized results for organochlorine pesticides

Compound	Minimum (µg/Kg)	Maximum (µg/Kg)	Mean (µg/Kg)	Detection over the quantification limit (34 soil samples)
4,4'-DDE	0,13	58,17	7,16	88%
4,4'-DDT	0,55	16,26	6,42	53%
Endosulfan_sulfate	3,66	9,08	7,11	9%
2,4'-DDT	0,25	1,69	0,97	6%
2,4'-DDE	0,11	0,11	0,11	3%



Contribution to DDT-DDE levels

LEVELS IN THE EBRO RIVER BASIN

Soil samples: summarized results for PAHs compounds

Compound	Minimum (µg/Kg)	Maximum (µg/Kg)	Mean (µg/Kg)	Detection over the quantification limit (34 soil samples)
Benzo(a)anthracene	0,11	23,73	4,97	100%
Chrysene	0,27	48,27	9,74	100%
Benzo(k)fluoranthene	0,33	17,09	4,29	100%
Indeno(1,2,3-cd)pyrene	2,27	465,28	111,79	100%
Benzo(b)fluoranthene	0,11	21,32	5,18	97%
Benzo(g,h,i)perylene	0,88	274,75	70,83	97%
Benzo(a)pyrene	1,18	291,82	42,73	85%
Dibenzo(a,h)anthracene	0,22	269,14	82,07	76%
Pyrene	0,62	37,43	6,94	74%
Fluoranthene	0,46	12,03	4,08	65%
Anthracene	0,01	9,13	1,29	65%
Acenaphtylene	0,02	2,35	0,58	59%
Acenaphtene	0,01	1,73	0,94	59%
Phenanthrene	0,34	14,45	4,00	53%
Naphthalene	0,01	0,04	0,02	32%

Operational monitoring

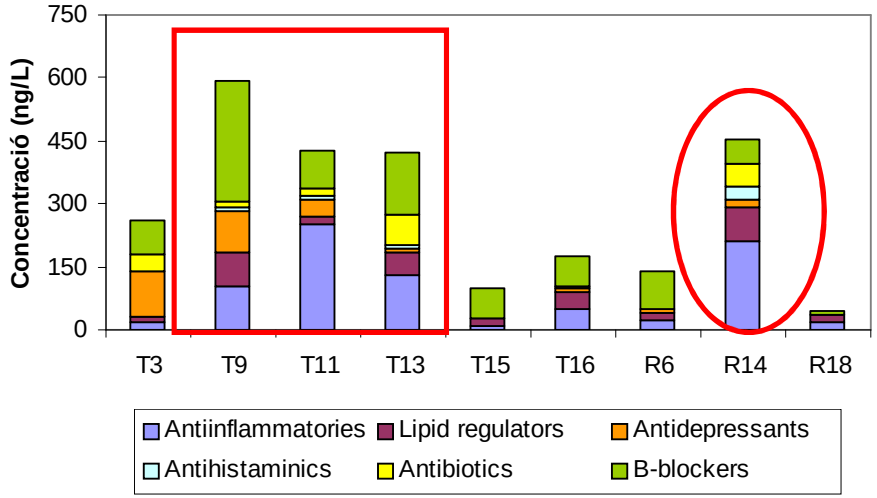
Operational monitoring (OM) will classify status of water bodies identified as being at risk of failing environmental conditions (**emerging contaminants**)

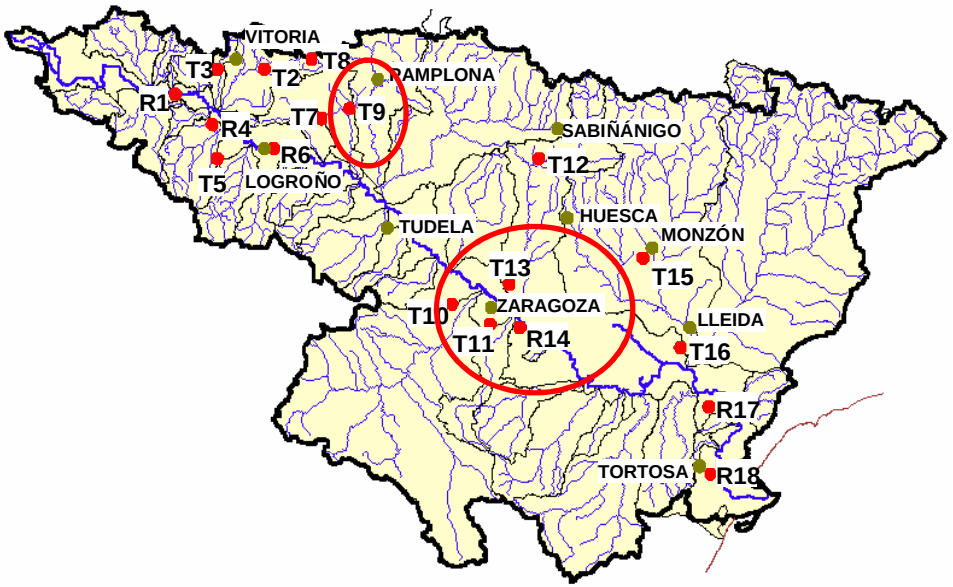
- *9 monitoring stations along the Ebro (surface water and sediment)*
- *6 wastewater treatment plants*

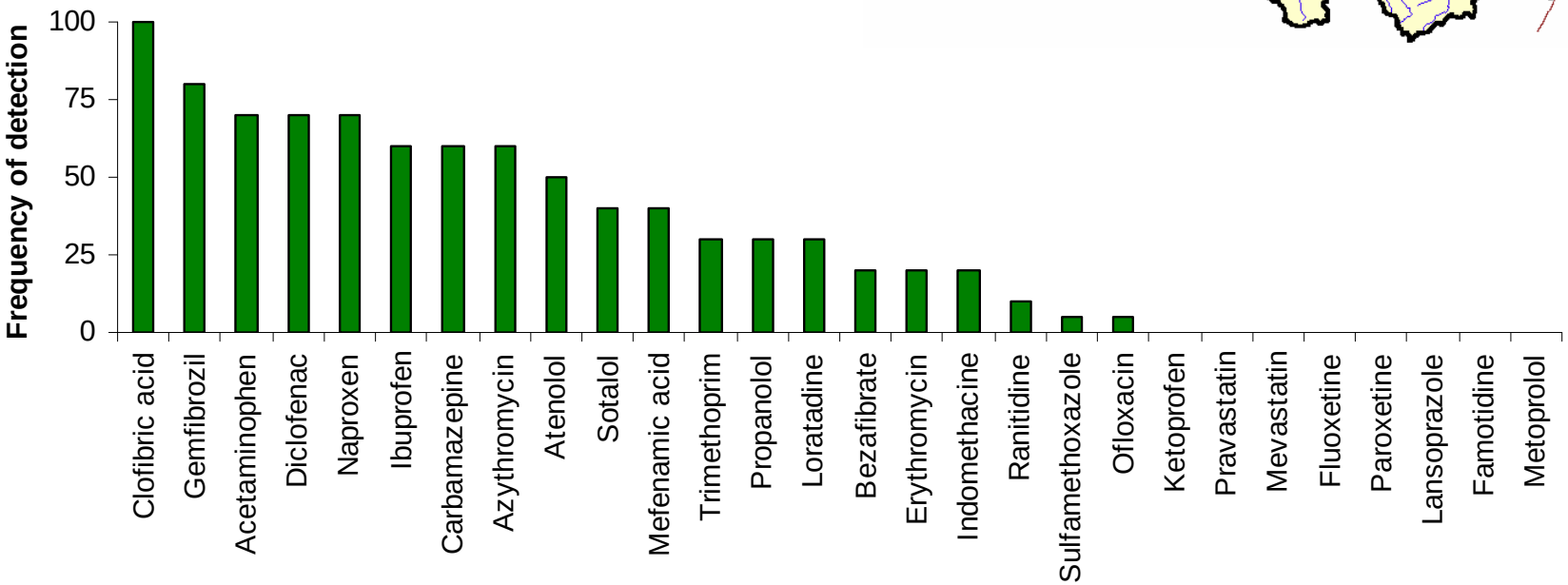
Target compounds

Analgesics and antiinflammatories	Lipid regulator and cholesterol lowering statin drugs	Psychiatric drugs	Antiulcer agents	Antibiotics	b-blokers
Ibuprofen	Clofibric acid	Carbamazepine	Lansoprazole	Erythromycin	Atenolol
Naproxen	Gemfibrozil	Fluoxetine	Loratadine	Azithromycin	Sotalol
Ketoprofen	Bezafibrate	Paroxetine	Famotidine	Sulfamethaxole	Metoprolol
Indomethacine	Pravastatin		Ranitidine	Trimethoprim	Propranolol
Diclofenac	Mevastatin			Ofloxacin	
Acetaminophen					
Mefenamic acid					
Propyphenazone					

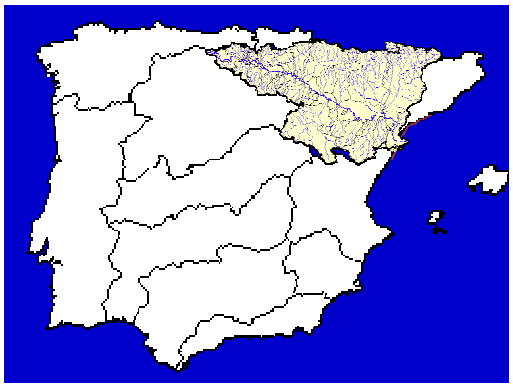
Screening of river waters

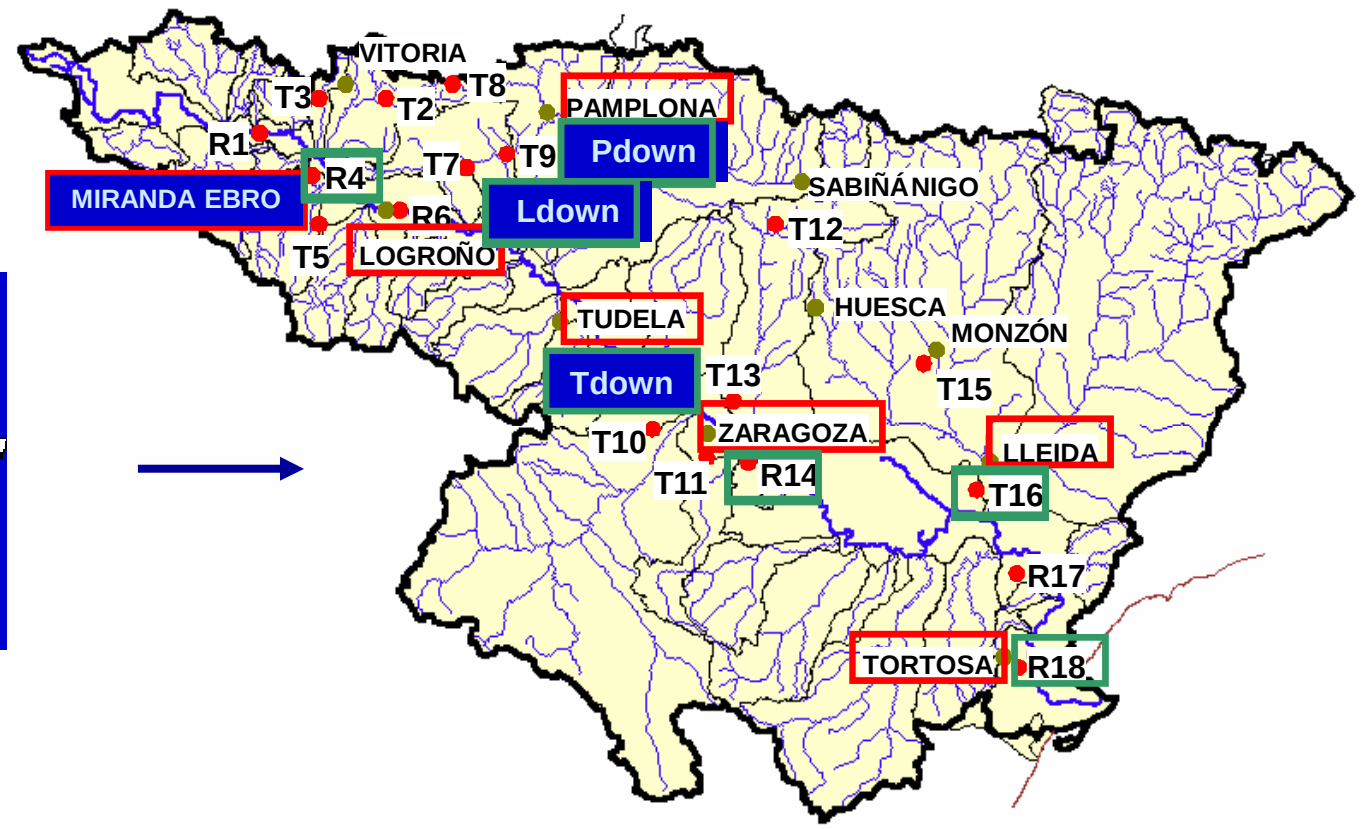






Contribution of WWTP to the presence of pharmaceuticals in receiving river waters





WWTP monitored: influent and effluent wastewaters

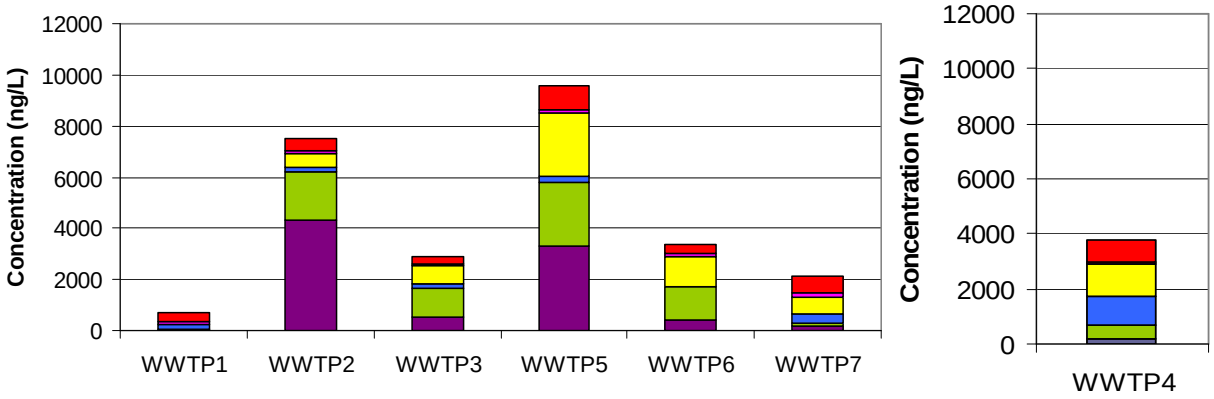
River water downstream the WWTP

Characteristics of the WWTP monitored

WWTP	Population	Flow rate (m^3/h)	Wastewtater treated	Hidraulic Rt (h)	Primary treatment	Secondary treatment
Miranda Ebro	52700	533	Urban	32	-	Activated sludge
Tudela	90000	833	Urban	18	Primary settling	Filters
Logroño	466560	2500	Urban and industrial	8	Primary settling	Activated sludge
Pamplona	773312	4313	Urban and industrial	25	Primary settling	Activated sludge
Zaragoza	835000	6833	Urban	10	Primary settling	Activated sludge
Lleida	180000	2917	Urban	6-10	Primary settling	Activated sludge
Tortosa	36625	305	Urban	33	-	Activated sludge

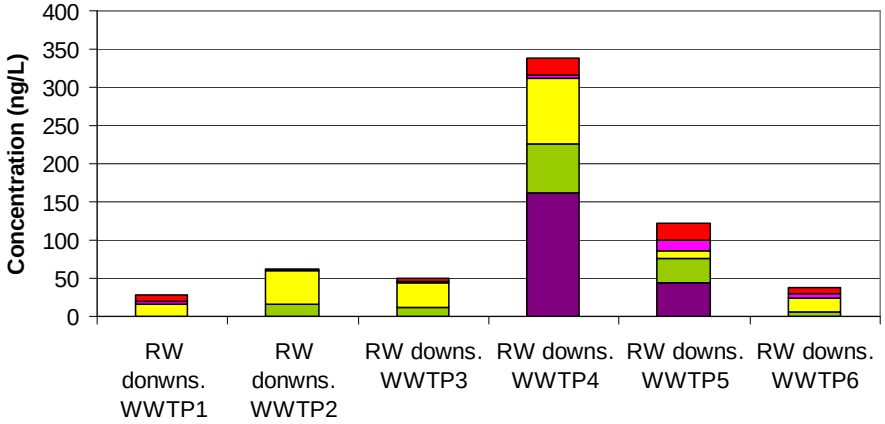
Contribution of WWTP effluents

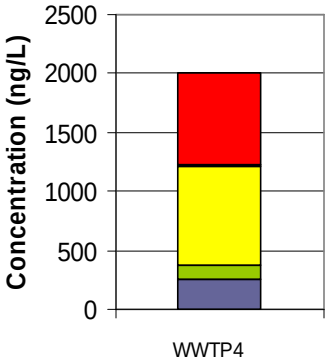
WWTP effluent



- There is an important **dilution factor**: Levels found in surface waters downstream WWTP are in the low ng/range, whereas in WWTP effluent concentrations of target compounds are between low µg/L-high ng/L range.

River water downstream WWTP



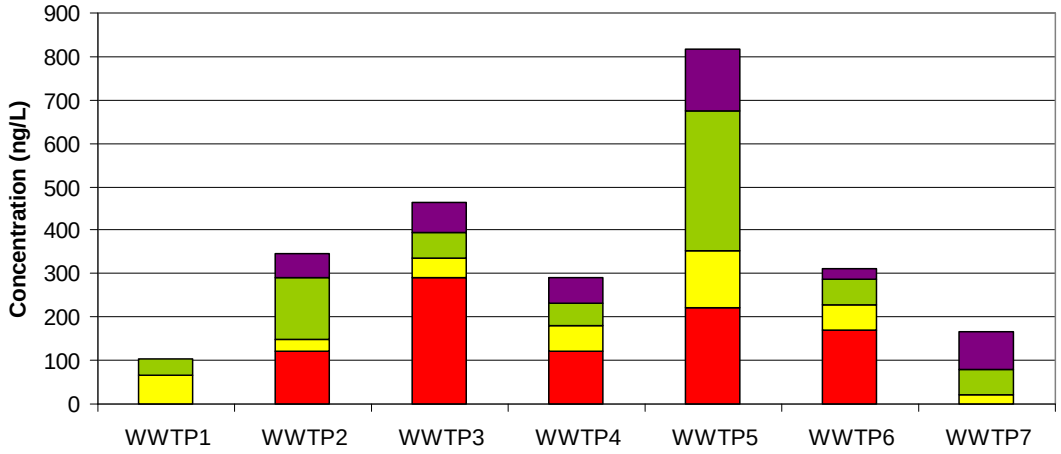


Environmental risks are reduced in river water due to the important dilution

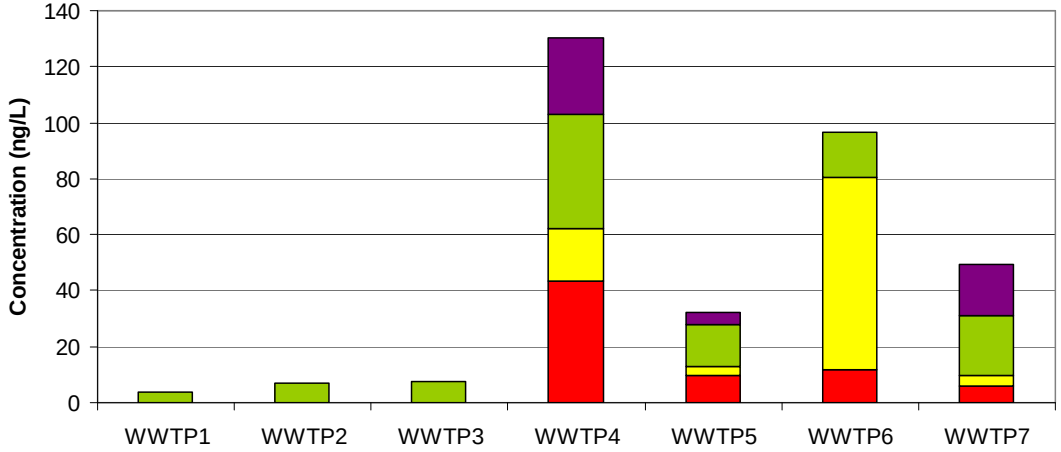
Atenolol **Gemfibrozil** **Diclofenac** **Naproxen** **Ibuprofen** **Carbamazepine**

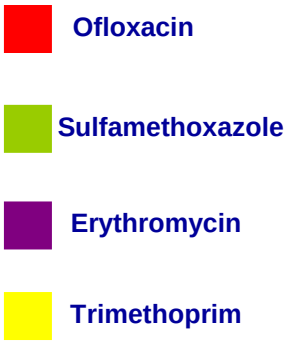
Contribution of WWTP effluents

WWTP effluent

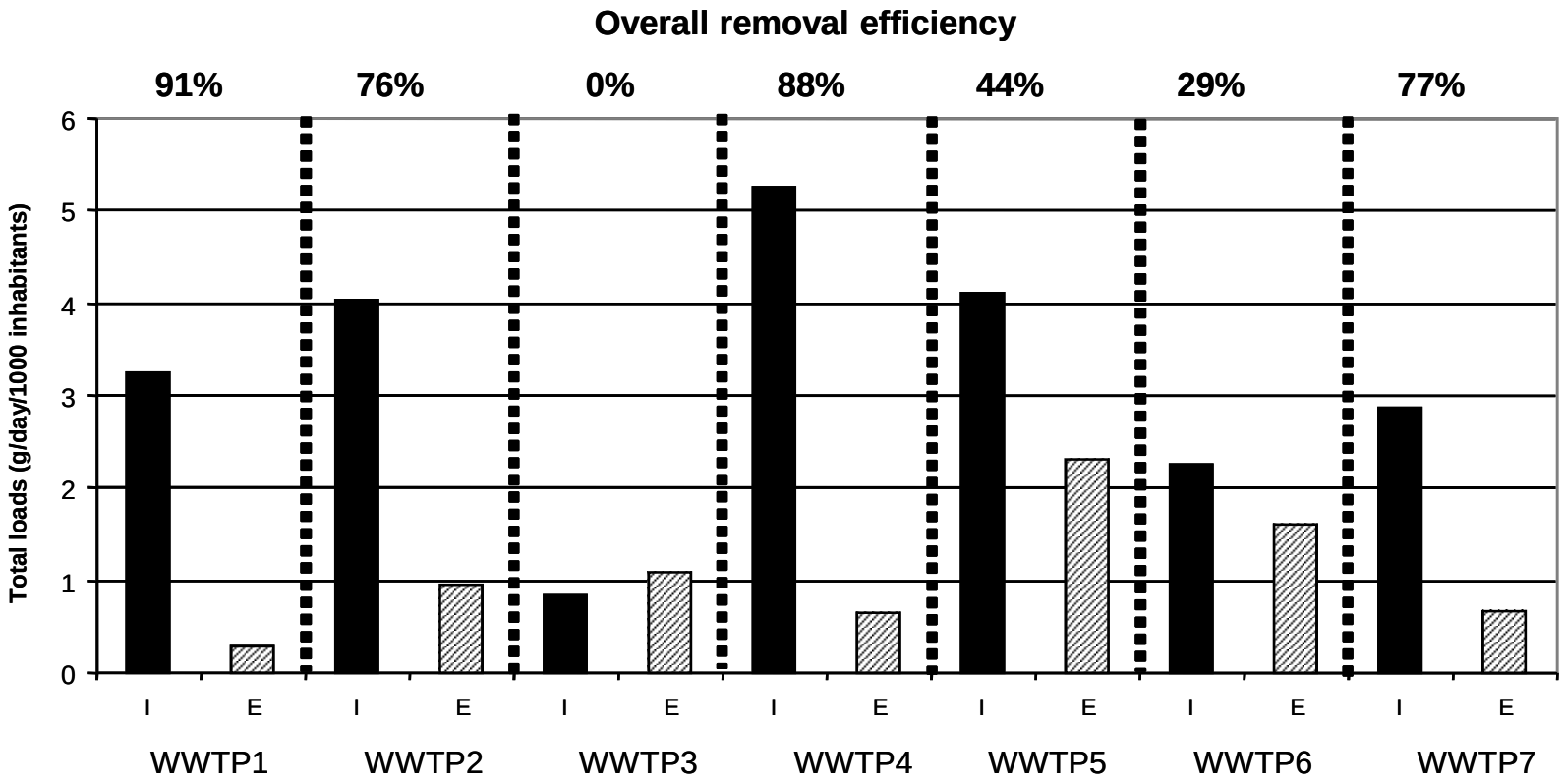


River water downstream WWTP





Removal efficiencies in WWTPs



Total loads of pharmaceuticals (June 2005) were normalized for population equivalents and expressed as g/day/1000 inhabitants

Investigative monitoring

Investigative monitoring (IM) , when SM shows that environmental objectives are not met or to assess the impact of accidental pollution events (priority pollutants + **emerging contaminants**)

19 sampling points in three polluted(Industry/Agricultural) zones:

Brominated flame retardants at risk zones Flix and Cinca - **industrial impact**

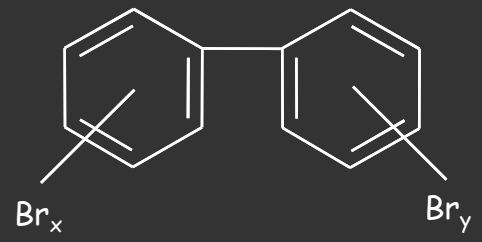
A) Regulated: Polybrominated diphenylethers (PBDEs) (from monoBDEs to decaBDE),

B) Non-regulados; Hexabromocyclododecane (HBCD) and Decabromodiphenyl ethane

Pesticides at delta Ebro – **agricultural impact**

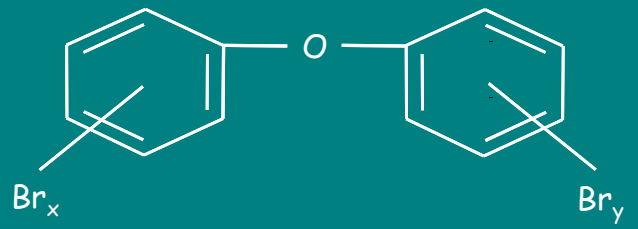
Brominated flame retardants: Chemical structures

Polibromobifenilos (PBBs)
209 congéneres



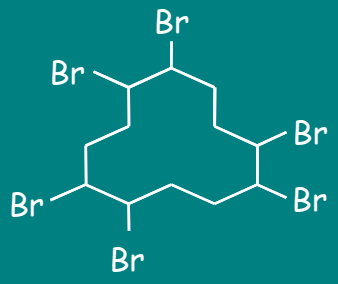
x + y = 1-10

Polibromodifeniléteres (PBDEs)
209 congéneres



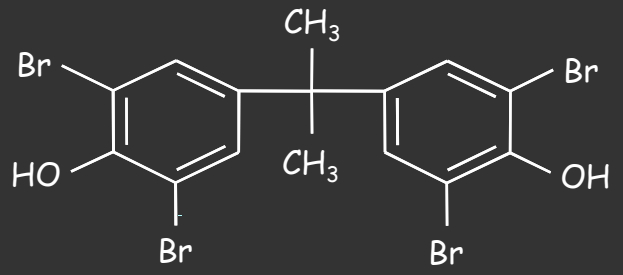
x + y = 1-10

Hexabromociclododecano (HBCD)
3 isómeros



α-HBCD β-HBCD γ-HBCD

Tetrabromobisfenol A (TBBPA)



VERO RIVER: Sediment

BDE-209 levels in **Sediment** samples collected near industry facilities.

Country	Sample	Maximum level (ng/g dw)	Ref.
Sweden	Sediment river with numerous textile industries	360	Sellström, 1998
United Kingdom	Sediment downstream areas of manufacturing plants	399	Allchin, 1999
The Netherlands	Suspended particulates from surface waters near a textile facility	4600	de Boer, 2003
Spain	**Sediment downstream a textile industry**	**5000**	**Our study, 2004**

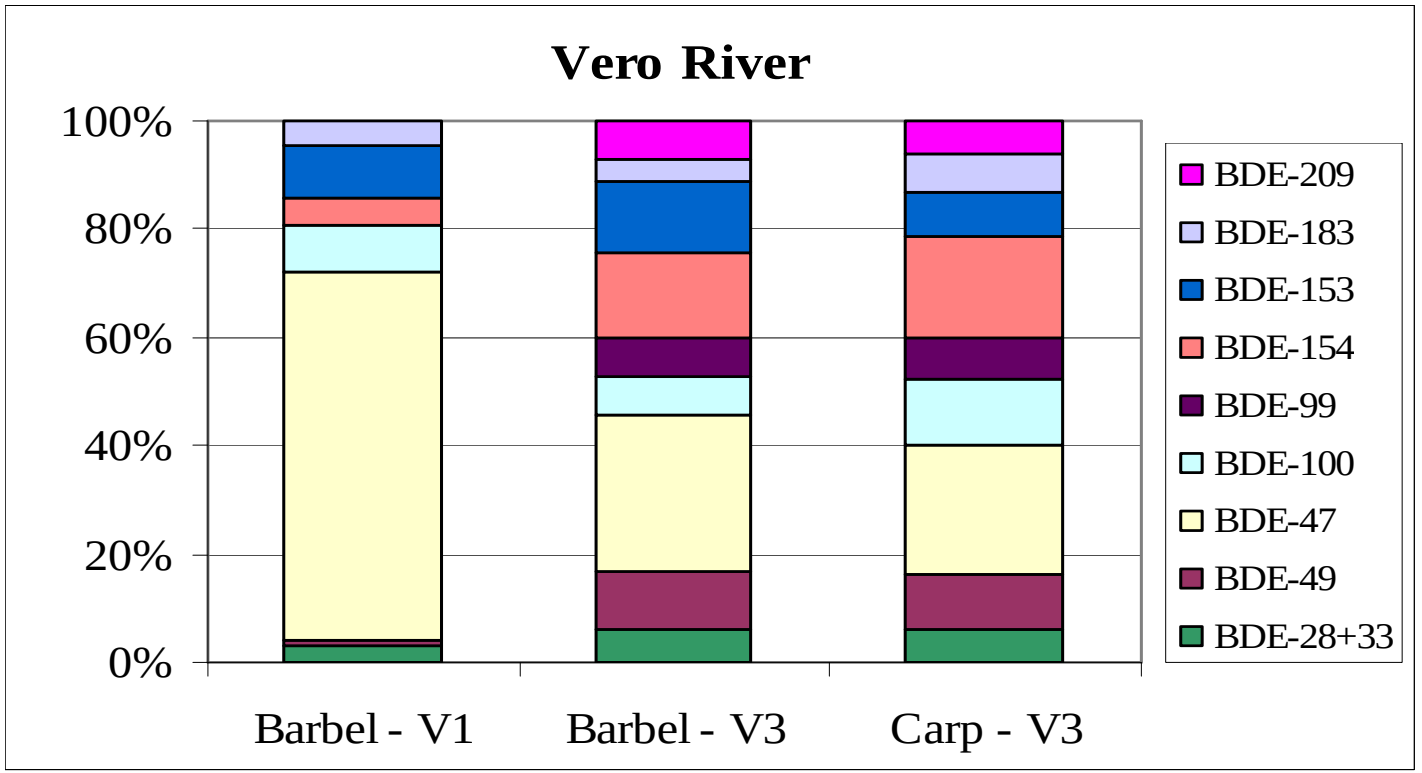
VERO RIVER: Biota

Summary of reported concentrations of **BDE-209** in aquatic biota.

Country	**Sample**	**Maximum level (ng/g lw)**	**Ref.**
Germany	Bream (*Abramis abrama L.*)	37	Lepom, 2002
Baltic sea	Pike (*Esox lucius*), perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*)	116	Burreau, 2004
North sea	Sole (*Solea solea*), bib (*Trisopterus luscus*) and whiting (*Merlangius merlangus*)	37	Voorspoels, 2003
Spain	**Barbel (*Barbus graellsii*) and carp (*Cyprinus carpio*)**	**63**	**Our study, 2004**

VERO RIVER: Biota

Percentage contribution of various congeners to the total PBDEs detected in muscle samples from the Vero River



Published studies with caged carps: **BDE-209** → **BDE-154**

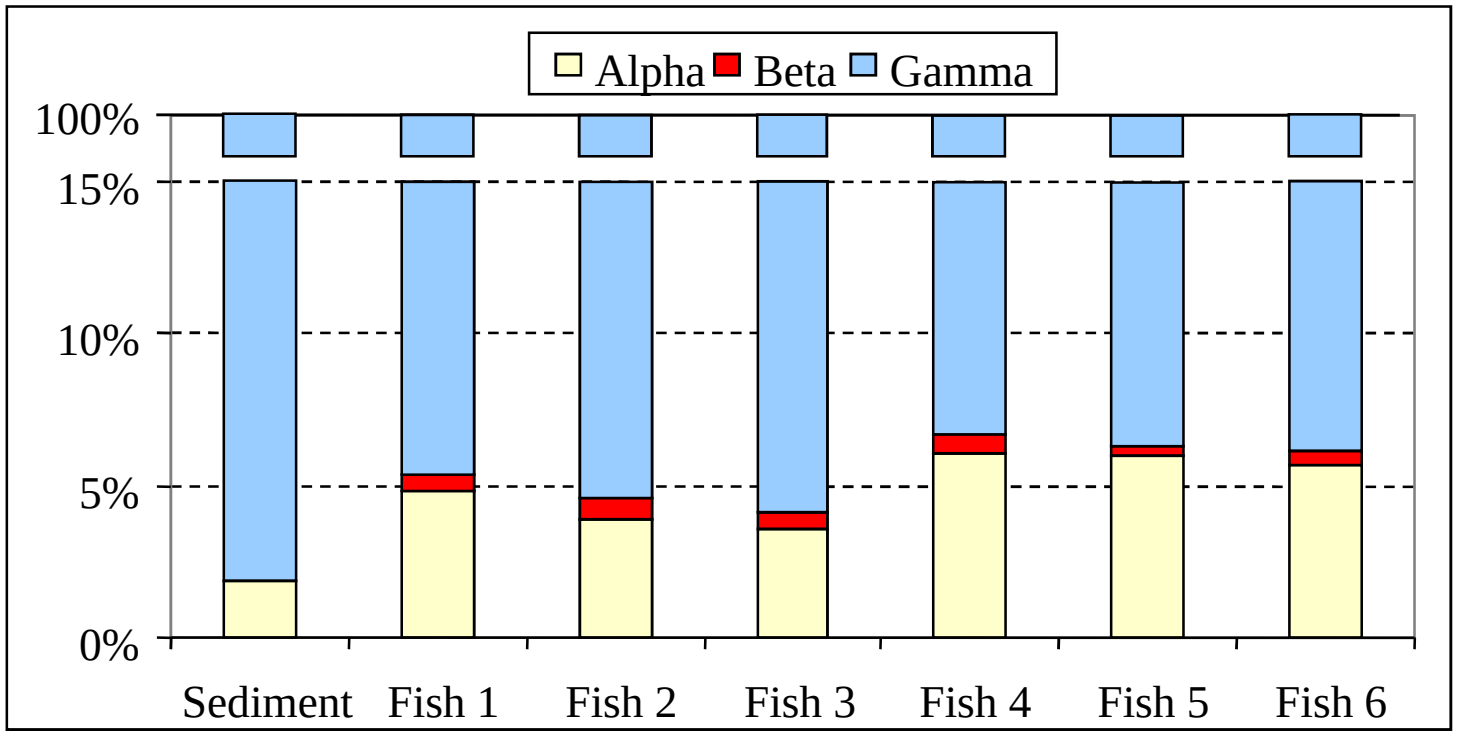
CINCA RIVER: Biota

Summary of reported concentrations of **HBCD** in European aquatic biota.

Country	**Sample**	**Maximum level (ng/g ww or lw)**	**Ref.**
UK (downstream manufacturing HBCD plant)	Trout	6760 (ww)	Allchin, 2003
	Eel	10000 (ww)	
Switzerland	Whitefish	210 (lw)	Gerecke, 2003
The Netherlands	Eel	93 (lw)	Morris, 2004
Sweden	Herring	180 (lw)	Remberger, 2004
Spain	**Southwestern nase**	**12408 (ww)** **104288 (lw)**	**Our study, 2004**

CINCA RIVER: Biota

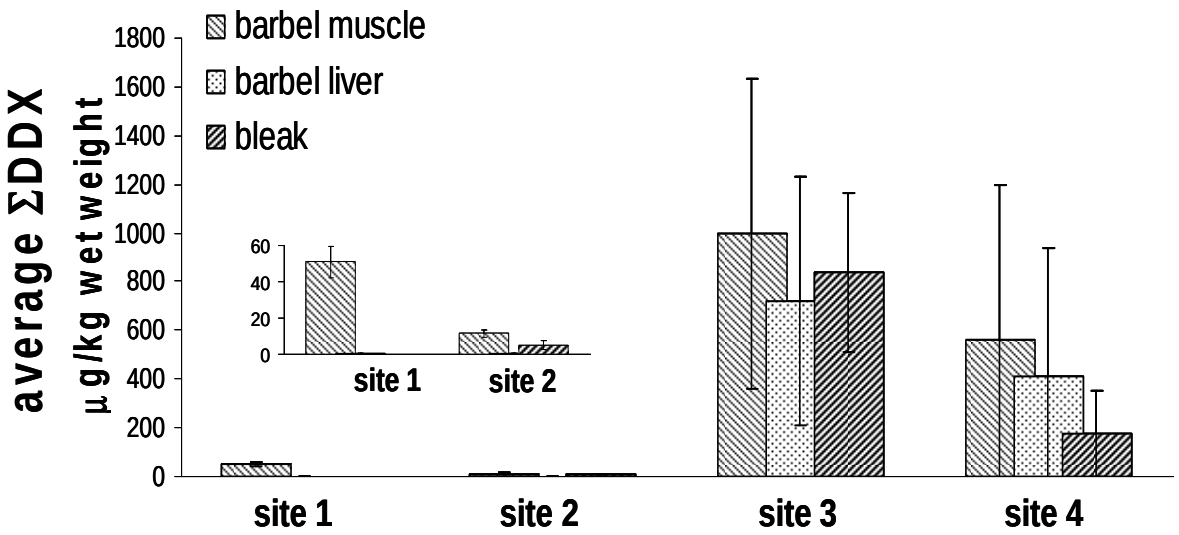
Percentage contribution of HBCD isomers in fish samples from the Cinca River (Site C4)



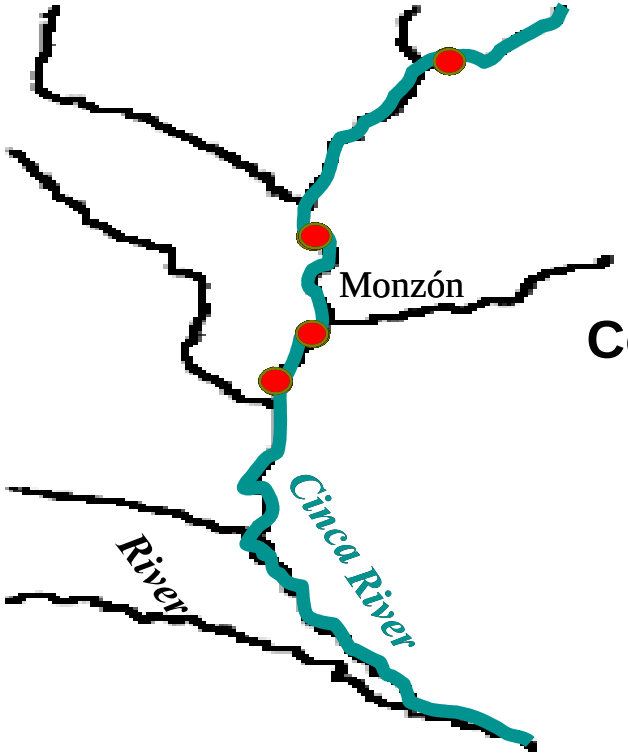
Published studies reported potential biotransformation of gamma to alpha. This study showed low biotransformation, probably due to a recent exposure.

CINCA RIVER: DDX CONTAMINATION

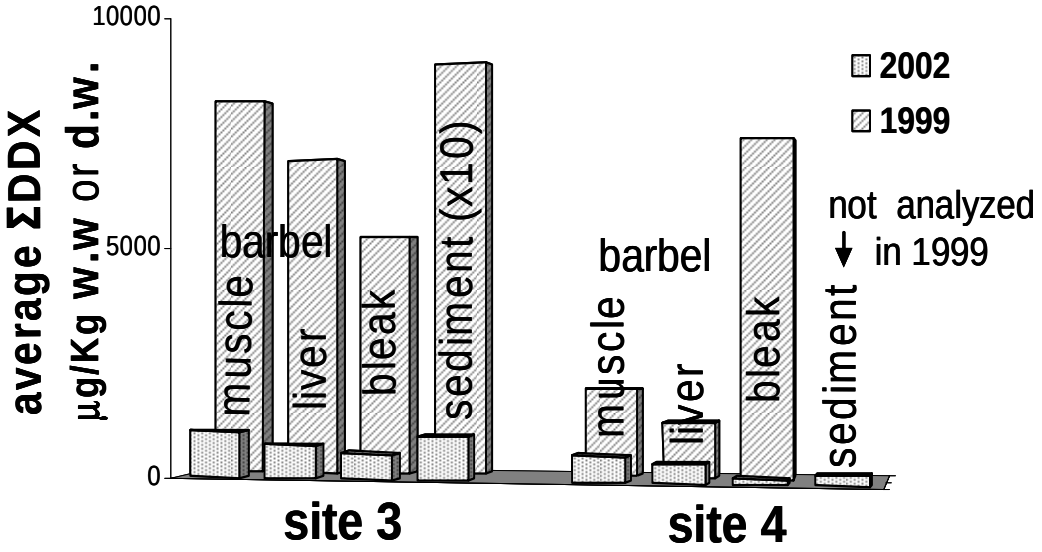
Average levels of ΣDDXs in fish (µg/Kg w.w.)



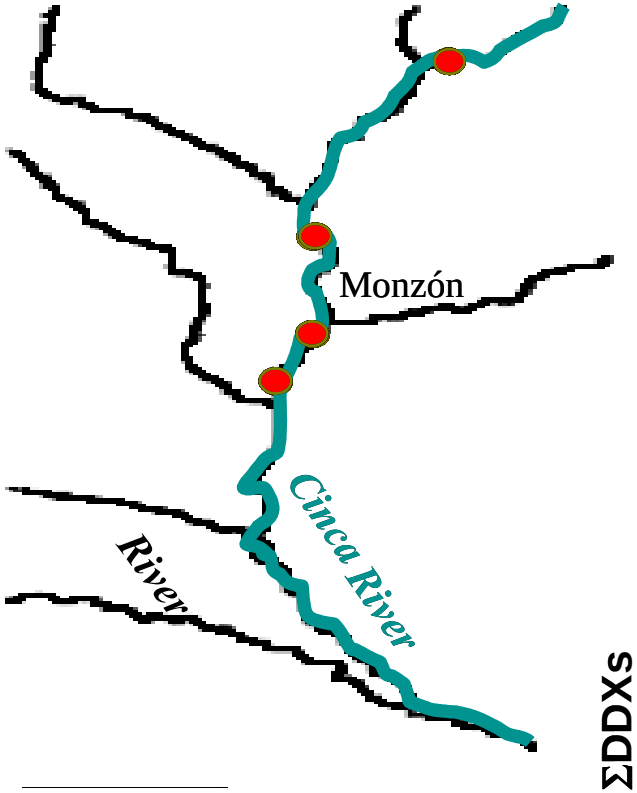
CINCA RIVER: DDX CONTAMINATION



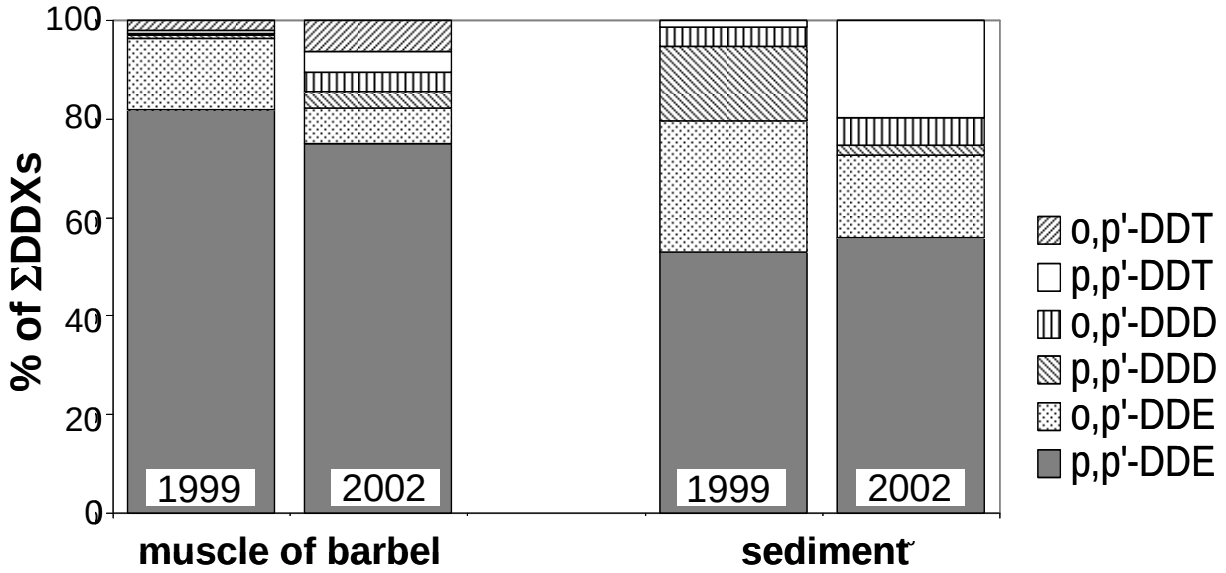
Comparison between this study (2002) and 1999
Data are expressed in μg/Kg w.w. in fish
and 10x μg/Kg d.w. in sediment.



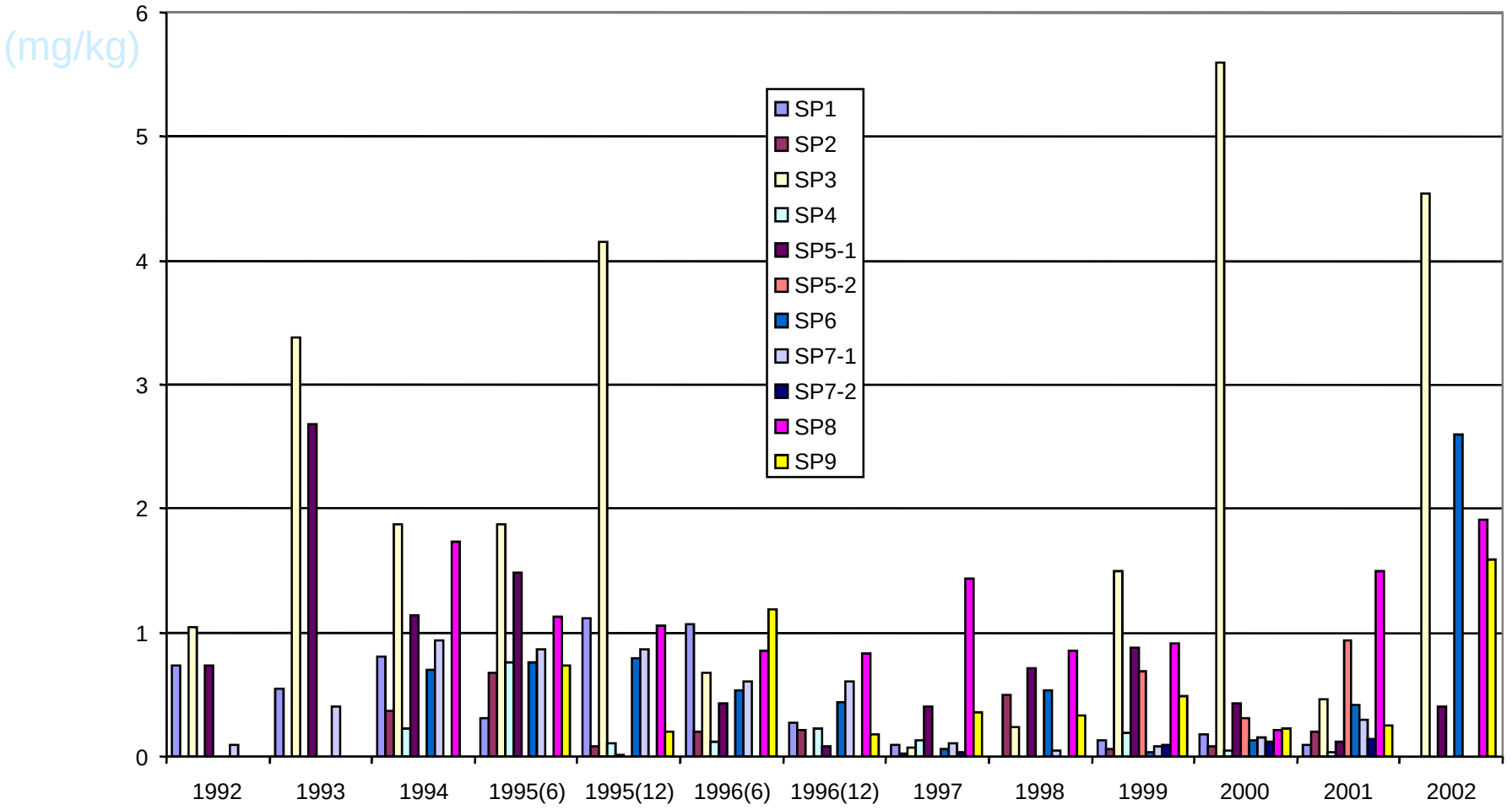
CINCA RIVER: DDX CONTAMINATION



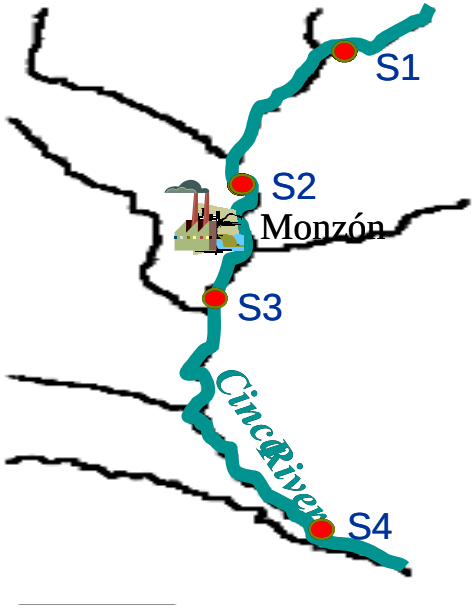
Percentage of the different compounds in muscle of barbel and sediment in site 3

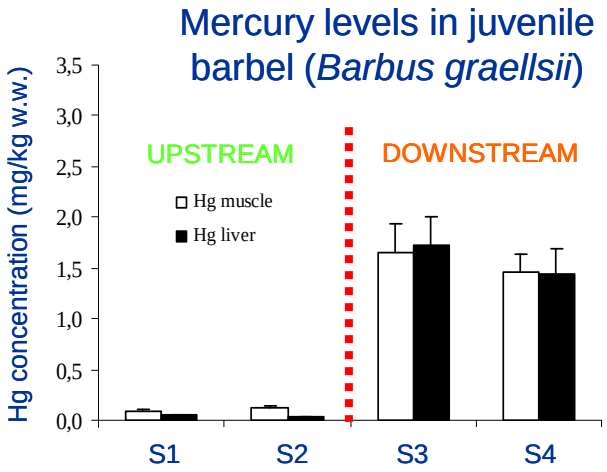


Pollution trends: Hg in sediments

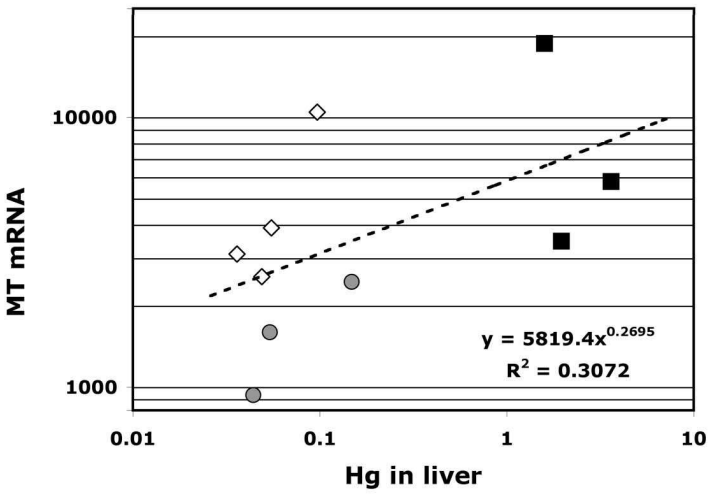


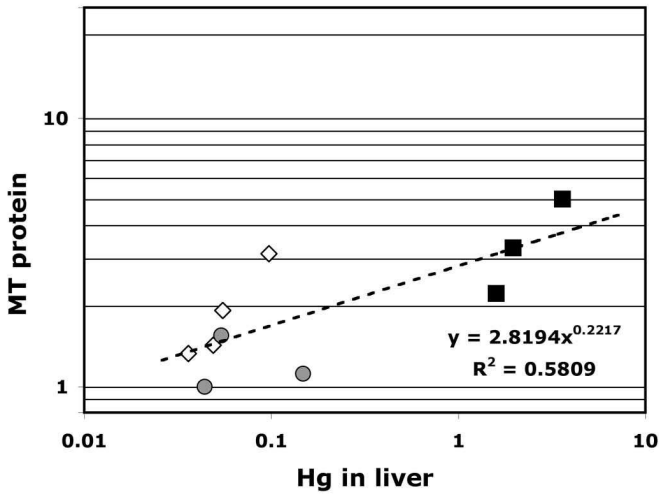
CINCA RIVER: Hg CONTAMINATION





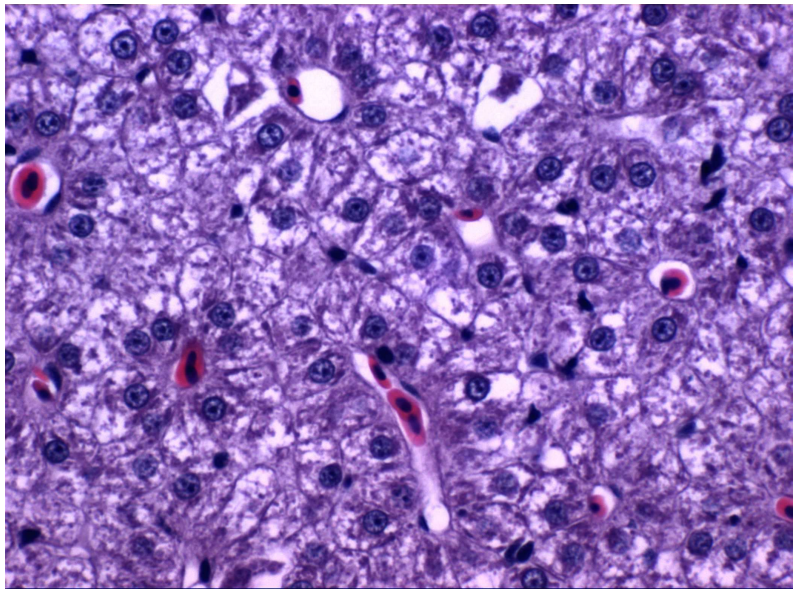
Barbel downstream of the chlor-alkali plant had very high mercury levels, and a good correlation was found between mercury levels and metallothionein, at mRNA and protein levels)



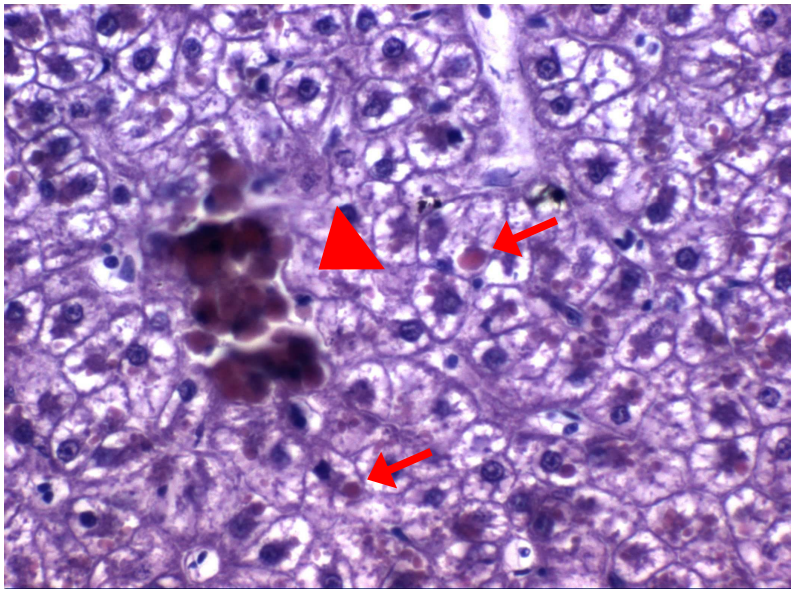


CINCA RIVER: Hg CONTAMINATION

Barbels with the highest Hg levels in the liver also showed the most severe pathologies, and the processes found were consistent with the pro-oxidant effect of heavy metals



Normal liver of barbel from upstream, showing the normal structure.

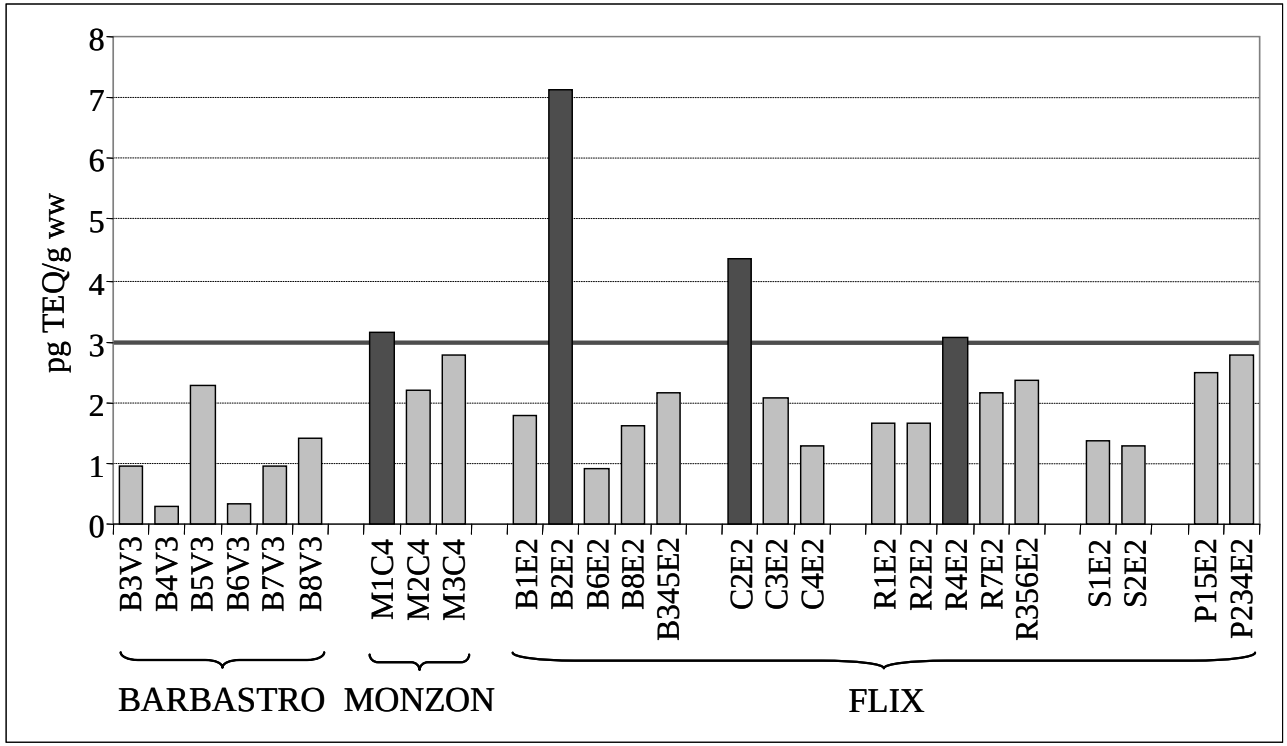


Lipofuscin in macrophage aggregates (arrowhead) and inside of the hepatocytes (arrows) in the liver of a barbel from downstream.

DIOXIN AND DIOXIN-LIKE PCBs

Dioxin and dioxin-like PCB results from the **Cinca and Flix risk zones**

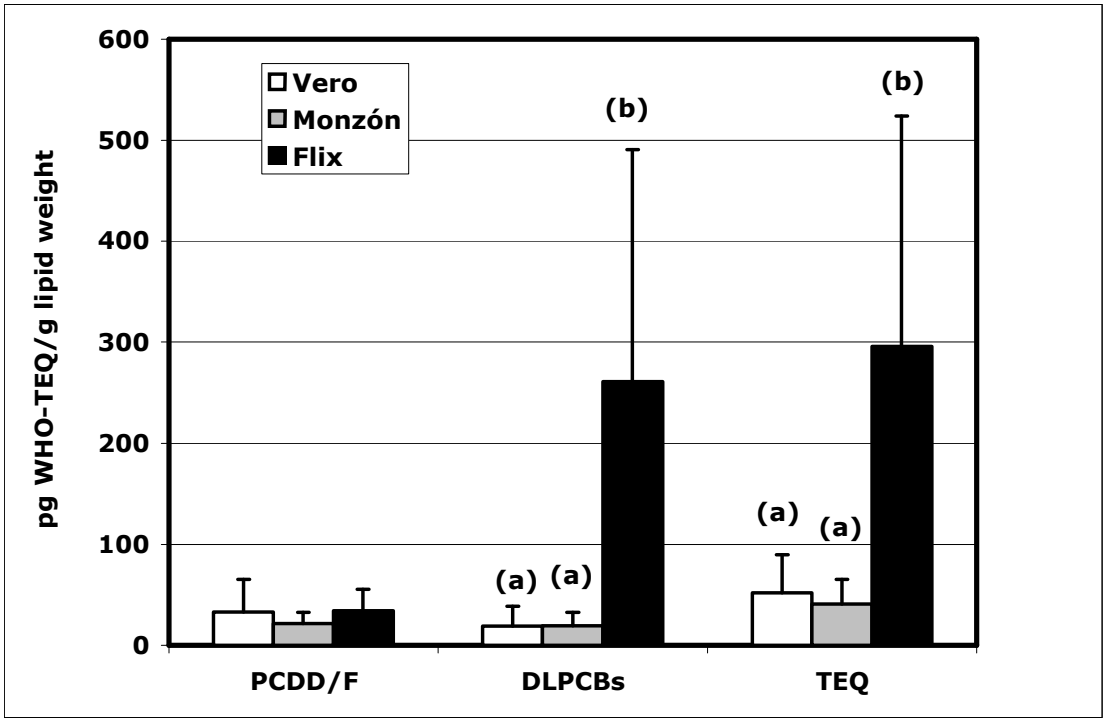
Total (PCDDs+PCDFs+dl-PCBs) TEQ values,
expressed in pg/g wet weight in different fish samples.
The European action level (**3 pg TEQ/g ww**)
is indicated as a darker horizontal line.



DIOXIN AND DIOXIN-LIKE PCBs

Dioxin and dioxin-like PCB contribution

Levels of PCDD/F, dl-PCBs and total TEQ
in fish populations from Barbastro, Monzón and Flix sites.
Values expressed in pg WHO TEQ/g lipid weight.
Bars represent means; lines indicate standard deviations.
Letters "a" and "b" indicate significant differences
between the populations (Tamhane test).



DIOXIN AND DIOXIN-LIKE PCBs

Biological response

CYP1A expression from barbel samples

Location	Sample	CYP1A1 wxpression[a]
Barbastro	B3V3	400 ± 100
	B4V3	0.5 ± 0.03
	B5V3	350 ± 20
	B6V3	1600 ± 100
	B7V3	800 ± 50
	B8V3	1.1 ± 0.09
Flix	B1E2	1000 ± 50
	B2E2	3600 ± 200
	B3E2	1100 ± 100
	B4E2	600 ± 200
	B5E2	700 ± 20
	B6E2	500 ± 40
	B7E2	3000 ± 150
	B8E2	2800 ± 200

[a]Expressed as mRNA copies of CYP1A per 1000 copies of β-actin mRNA;
Mean and SD from three technical replicates.

DIOXIN AND DIOXIN-LIKE PCBs

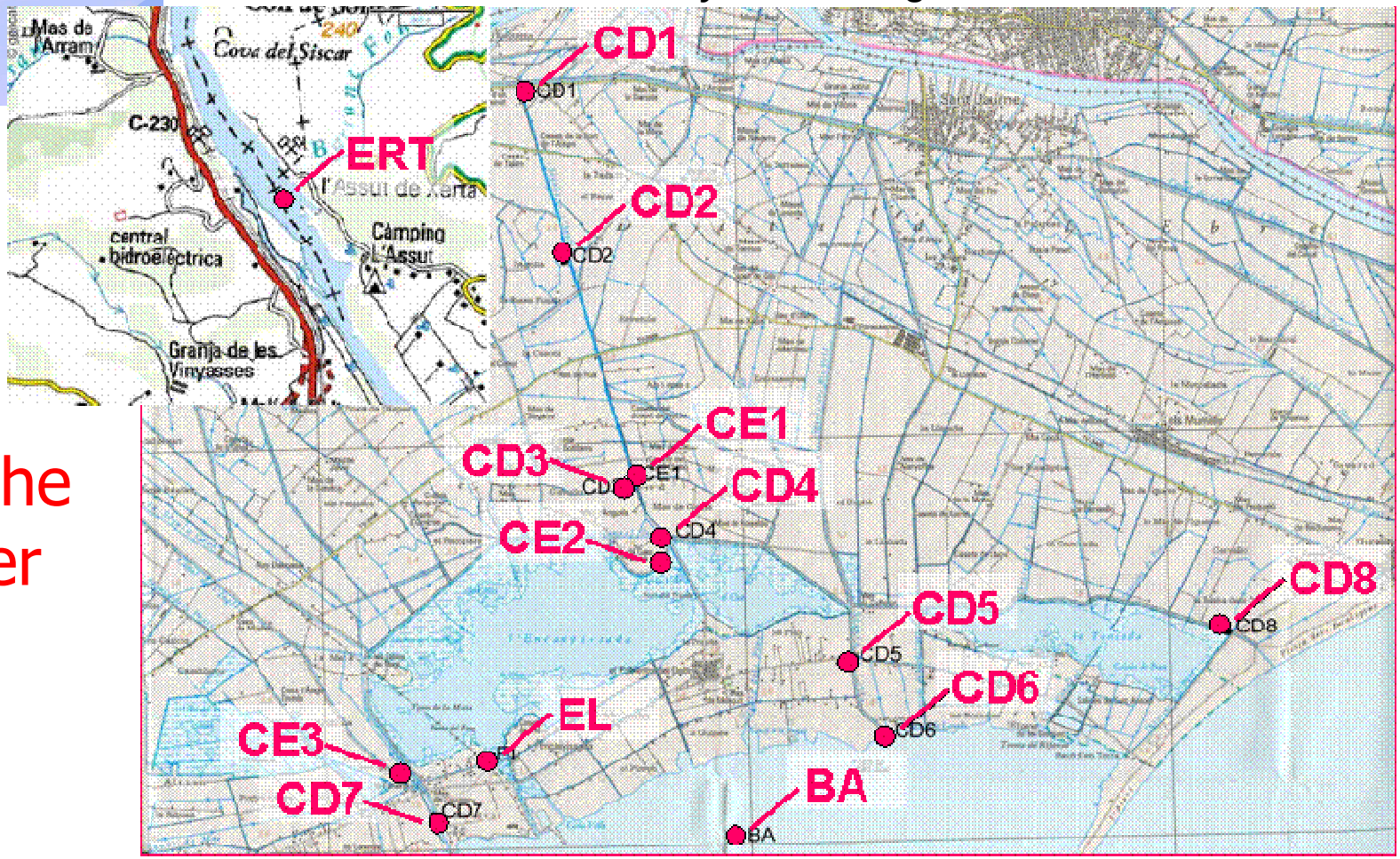
Biological response

Linear correlation parameters between CYP1 expression levels
(expressed as mRNA copies per copy of ßActin mRNA)
and levels of PCDD/F, DLPCBs and total TEQ
(expressed in pg WHO-TEQ/g lipid weight)
for *Barbus graellsii* samples from Vero and Flix sites

Parameter	*n*	R	*p* value
PCDDs/Fs	11	-0.366	0.264
dl-PCBs	11	0.720	0.010
Total TEQ	11	0.643	0.029

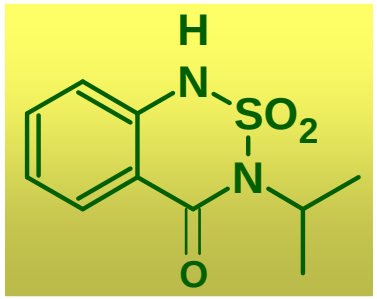
Polar pesticides

ERT, river upstream of Delta
CD, drainage channels
CE, irrigation channels
BA, Alfacs Bay
EL, Encanyissada Lagoon

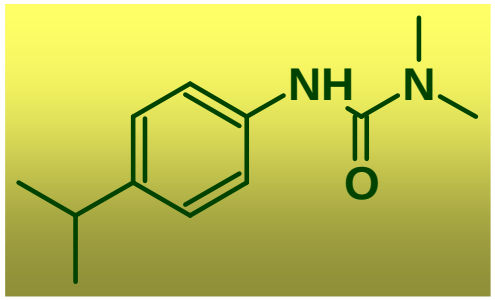


Delta of the Ebro river

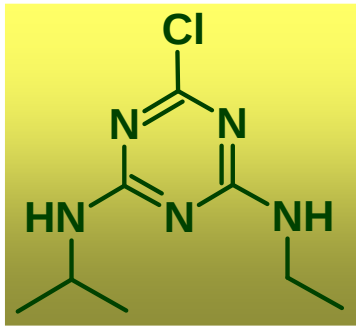
Target pesticides



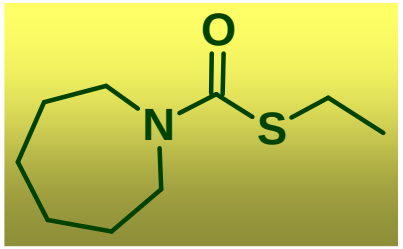
4 acidic pest.
(bentazone)



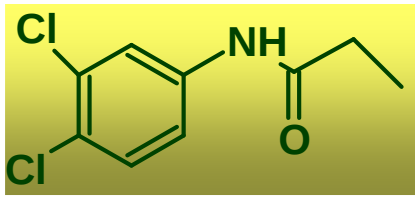
4 phenylureas
(isoproturon)



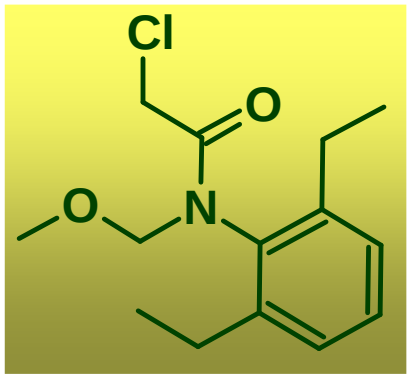
6 triazines
(atrazine)



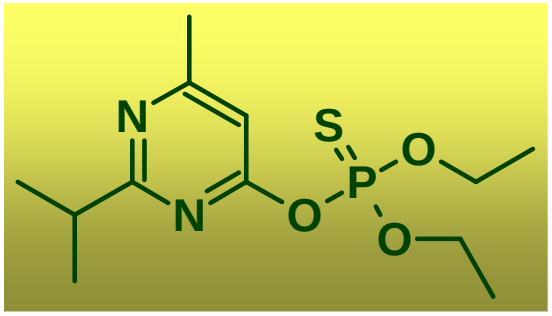
1 thiocarbamate
(m*olinate*)



1 anilide
(propanil)



2 chloroacetanilides
(alachlor)



4 organophosphates
(diazinon)

Levels (in µg/L) of pesticides in water

Pesticide	Max. Conc.	AVG (%P)
Cyanazine	n.d.	- (0 %)
Chlortoluron	0.003	0.002 (6 %)
Isoproturon	0.007	0.002 (92 %)
Mecoprop	0.026	0.008 (92 %)
Metolachlor	0.027	0.016 (8 %)
Diuron	0.036	0.014 (92 %)
Diazinon	0.044	0.005 (98 %)
2,4 D	0.172	0.024 (90 %)
Malathion	0.218	0.218 (2 %)
Simazine	0.376	0.048 (98 %)

Pesticide	Max. Conc.	AVG (%P)
Fenitrothion	**0.681**	**0.313 (24 %)**
Molinate	**0.849**	**0.217 (86 %)**
Atrazine	0.901	0.314 (100 %)
MCPA	**13.90**	**1.877 (100 %)**
Propanil	**16.82**	**0.948 (90 %)**
Alachlor	62.90	17.79 (16 %)
Bentazone	**126.8**	**30.51 (100 %)**

Levels of pesticides in sediments of the Ebro river delta

Compound	Concentration in ng/g		
	Min.	Max.	Average
Bentazone	0.9	21.1	7.7
Propanil	0.2	4.1	2.0
Atrazine	0.9	2.8	2.0
Deisopropylatrazine	0.6	7.9	2.0
Desethylatrazine	0.3	3.2	0.6
Diuron	0.5	2.8	1.4
Metolachlor	4.8	29.0	13.9

Biomarkers

I) DAPHNIA: *pools of 10 adults*

√ Inhibition of acetyl and carboxyl cholinesterase activity
√ Oxidative stress biomarkers: CAT, GST
√ Feeding rate: High ecological relevance

II) CORBICULA: 10 *pools of gills or digestive gland from 3 animals*

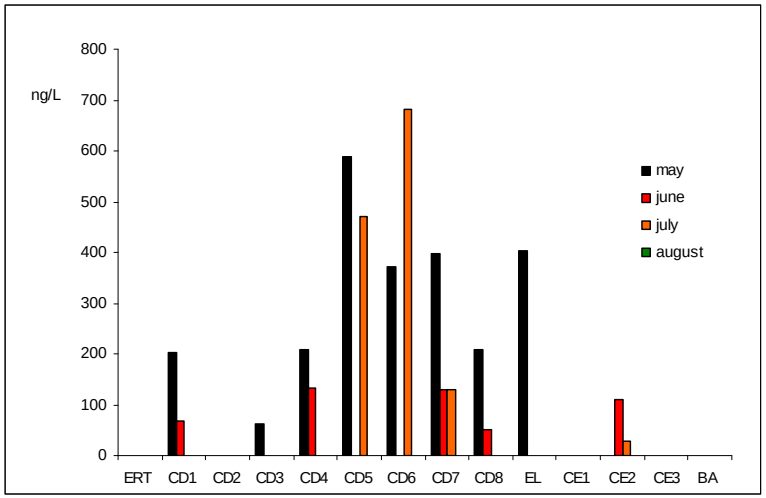
√ AChE (gills)
√ CAT, GST, GPX, SOD, Lipox (DG)
√ Histopathology
√ Filtration rate????

III) MUSSELS: 10 gills or digestive glands

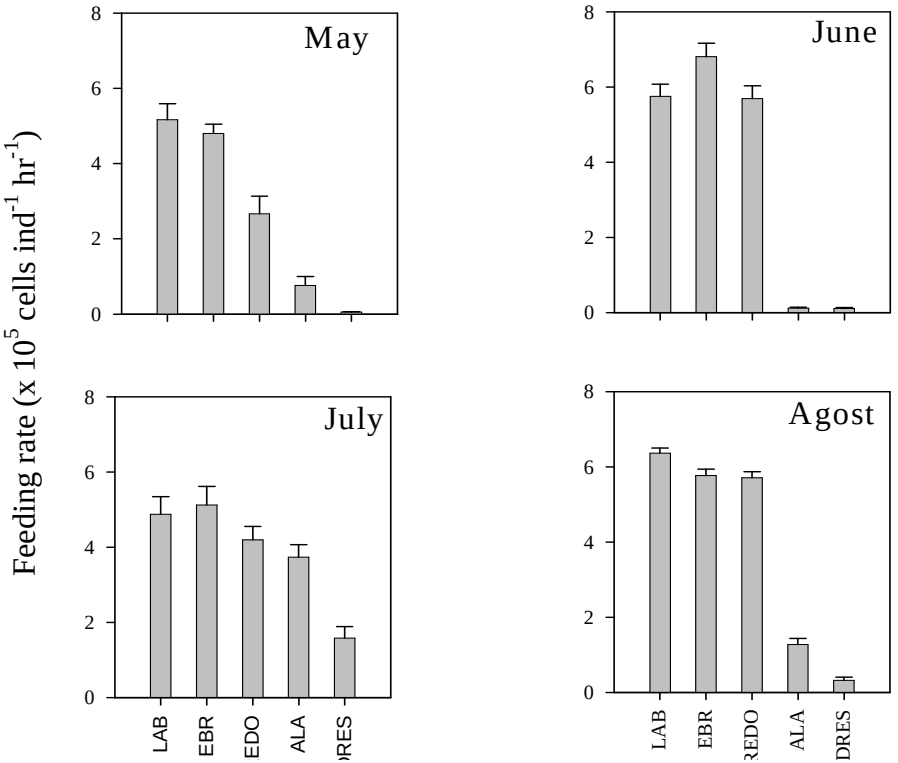
√ AChE (gills)
√ CAT, GST, GPX, SOD, Lipox (DG)

Fenitrothion

- √ Detected at high levels in May (CD5, CD7, CD8) and July (CD5, CD7)
- √ Fenitrothion concentrations at CD5 in May and July are near the 48-h LC50 in *Daphnia magna* (500 ng/L)
- √ The high variability found suggests sporadic high level applications instead of systematic applications



FEEDING


Feeding rate (x 10^5 cells ind^-1 hr^-1)
May
June
July
Agost
0
2
4
6
8
LAB
EBR
EDO
ALA
RES

CONCLUSIONS

Brominated flame retardants

-Two high contaminated areas were found along the Ebro River: the first one showed a high HBCD contamination, and the second one presented high contamination of deca-BDE-209. In both cases, the industry responsible of the contamination was identified.

-Analyses of biota samples showed that both contaminants, HBCD and deca-BDE-209, are bioavailable.

Dioxin-like compounds

-Dioxin-like compounds were analysed in different sites with different historical pollution records.

-Results indicated significant accumulation of dioxin-like PCBs in samples at the Flix site. Concomitantly, cytochrome p450 1A (CYP1A) expression, a known indicator for dioxin-like pollution, was significantly elevated in barbel from the Flix site.

-Our study suggest a significant biological impact at the Flix site, closely related to the presence of dioxin-like PCBs, whereas the PCDDs/Fs contribution to this impact appears to be non-significant.

DDXs

-DDT pollution was detected in sampling sites downstream a factory manufacturing dicofol. However, levels have dropped since a previous study in 1999.

Mercury

-High mercury levels were found in fish downstream of a cholr-alkali plant placed in the Cinca river.

-Good correlation was found between the mercury levels in liver and toxicological effects at different organisation levels: mRNA, protein and cellular.

CONCLUSIONS

Pesticides

- Distribution of organophosphorus insecticides and herbicides in groundwater of the Ebro river basin was very much dependant on the sampling location due to the specific usage pattern in each area.
- For pesticides hot spot areas identified are Zaragoza area, Segre and Gallego catchmen). More intensive agricultural exploitations showed higher degree of pollution while little orchards showed more variability.
- No significant temporal trends were found. DEA in water and DDE in soil were the main degradation products found and their concentration was always higher than the parental compounds.

Pharmaceuticals

-Total loads ranged from 2 to 5g/day/1000 inhabitants and from 0.5 to 1.5g/day/1000 inhabitants in influent and effluent wastewaters, respectively.

-High removal rates in WWTP were mainly achieved for analgesics and anti-inflammatories, while the other groups showed lower rates, ranging from 20 to 60%. The antiepileptic carbamazepine was not eliminated at all in most cases.

-Due to this fact, WWTP effluents are major contributor of pharmaceuticals in the river water.

Management of the monitoring data at CHE (Ebro)

1. Priority (regulated) substances

- Diffuse pollution (agriculture) not much is done. Ebro river basin is managed by CHE-Ministry of Environment, but agriculture is another Ministry
- Urban pollution - Waste Water Treatment Plants (e.g. nonyphenol)- actions coordinated with Regional Water Agencies (Agencia Catalana de l´Aigua)
- Industrial pollution, like Hg , DDT and brominated flame retardants, HCBD. The industry is known- chemicals from manufacture-but although regulatory action is slow (many socio-economic interests) it will happen

2. Emerging (non regulated) substances (i.e. Pharmaceuticals)

- Separate treatment of “hot spots”: hospital wastewaters (drugs)
- For drugs recommended actions are: Labelling (Sweden), urine separation, more environmental education (25-33% of drug disposal as household waste or directly to toilet) but still 1 dollar spent on drugs can save 6 dollars in hospital costs

Issues to be considered for monitoring and managing river pollutants- examples

1. Knowledge transfer from fundamental science-*understanding the processes*- to applied science ? And what about regulatory issues ? What is the "delta value" of EU funded research projects to WFD at river basin scale ? Are river basin managers "intertested" in the outcome of the R& D results, i.e.g advance monitoring schemes ? How to motivate them?
2. Risk at the River basin should be based on EQS or should we consider further scientific achievements ? What about *Known Unknowns*, for instance , pesticide metabolites (present at EPA list but not at EU-WFD list)
3. *Source control/ reduction of chemicals key issue*. Expected benefits: overall reduction on exposure to dangerous substances, improvement of biodiversity, reduced costs in WWTP, reduced potential of accumulation of dangerous substances in irrigated crops, improved soil quality, etc. Monitoring should make clear point vs diffuse sources.
4. Monitoring and assessemnt tools: we should know their "*window of operation*", Need of "quick scans " assessment (accuracy and precision needed too)

Long-term vision. Identification of ecological questions to improve river basin management

1. **Ecosystems services.** Benefits that the people obtain from the ecosystem. Provisioning services (food, water), regulating services (flood, disease control) cultural services (recreational, cultural benefits) and supporting services (nutrient cylcing) .Which components are essential for providing valuable services?
2. **Pollution at the River basin** .How catchment management can be used to reduce reduce diffuse pollution ? Deposits of sewage sludge on the agroecosystem ?
3. **Climate change.** What time lags can be expected between climate change and ecological change ? Which species are the best indicators of the effects of climate change on natural communities ? Changes in precipitation, impacts on water quality and quantity
4. **Energy**. What are the consequences of biofuel production for biodiversity at field, landscape and regional level ? **How sustainable** it is the situation in Spain (1kg corn needs 769 liters of water), with 561.000 Ha of corn-Atrazine in corn,0.44 kg/Ha (246 Tons) (1 Ha needs 7.200 m3/ 9.400 kg corn) that will need 3000 Hm3/year- this amount is higher than the human water consumption in Spain 2600 Hm3/year) and 3 times the PHN (Transfer Ebro/Andalucia)

ACKNOWLEDGEMENTS

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EU project

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