# Presencia de pesticidas y origen de nitratos y amonio en las aguas del Bajo Llobregat

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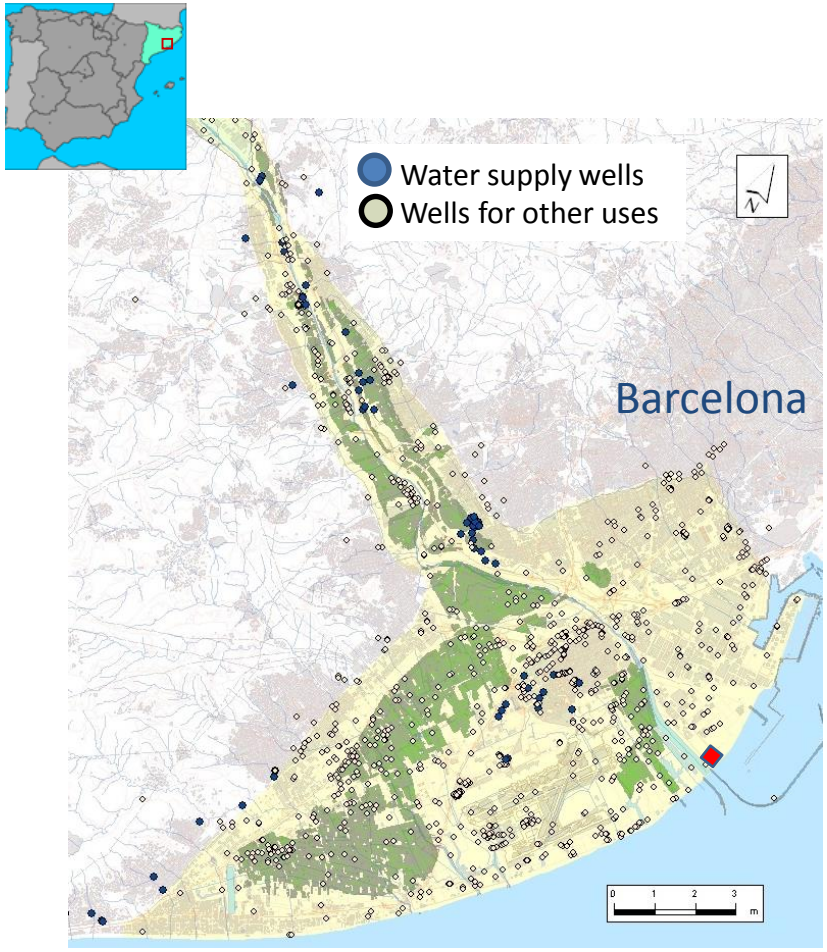
# ES ACTION LAB – BAIX LLOBREGAT CATCHMENT




***Location of groundwater wells***

- *Area with **multiple pressures**: urban (metropolitan area of Barcelona), agricuture, industry.*
- *Historical **contamination** by nitrates, ammonium, pesticides and other emerging contaminants.*
- ***Water scarcity**:*
  - *Mediterranean climate: low flows during normal conditions and peak events of either dryness or flooding*
  - *High demand of water resources.*
    - *>700 wells for drinking, agricultural, and industrial uses (50 $Hm^3$/year)*
    - *Llobregat River for drinking water (100 $Hm^3$/year)*
    - *Diverted Ter River water and desalinated water also used for drinking water production*
    - *Reclaimed water for irrigation, cleaning or aquifer recharge.*



This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No. 727450

***In a previous stage of the project:***

- *description of the site,*
- *revision of the water quality monitoring programs in place in the area (who, what, how),*
- *establishment of the structure of the harmonised dataset to be constructed,*
- *identification of information gaps regarding water quality, and the*

*Design of a **monitoring plan** to fill these gaps in the frame of WaterProtect (May 2018, deliverable D3.1)*



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***Questions that needed answers:***

- *How is the quality of the water used for abstraction of drinking water, irrigation, industrial and/or urban use?*
- *Which are the most critical pesticides?*
- *Do these pesticides comply with the legislation requirements in surface and groundwater?*
- *How contaminated are the river sediments?*
- *Do river sediments represent a risk for the aquatic organisms?*
- *Are river sediments a source of pollutants for drinking water resources in the area?*
- *What is the origin of nitrates pollution in the area?*
- *What treatments could be put in place in the area for pesticide pollution bioremediation?*
- *Could regenerated wastewater help protect drinking water resources?*

*Quintana et al. Sci. Total Environ 692, 952-965, 2019.*



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# WP3 - PARTICIPATORY MONITORING

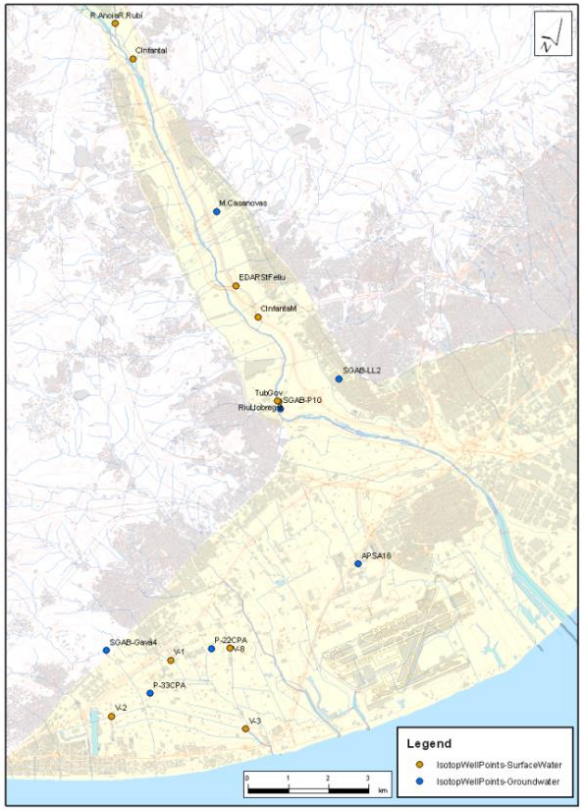
***Specific monitoring plan*** *designed in the framework of WaterProtect to:*

→ *fill information gaps:*

- *Pesticides (up to 108) in areas where they were not previously monitored with focus in surface water (3 campaigns)*
- *N, O, B isotopes to identify the origin of nitrate/ammonium (agriculture, livestock, urban sewage network)*

→ *investigate new bio-remediation techniques:*

- *Microalgae (INCOVER project)*
- *Fungi (BECAS project)*



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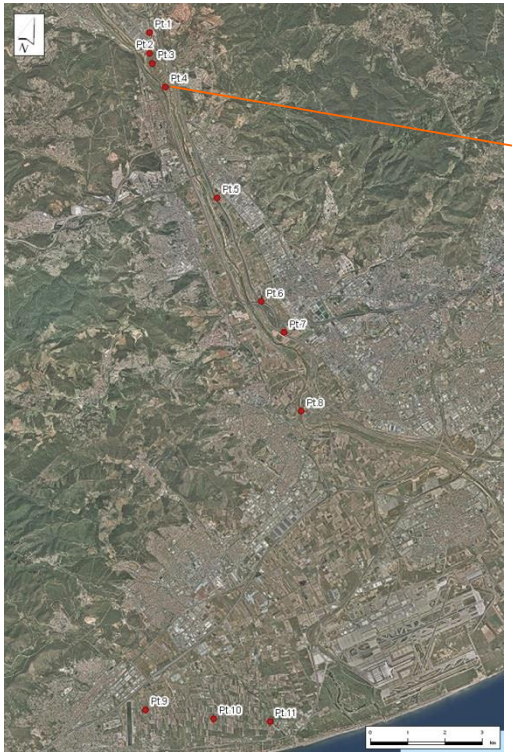
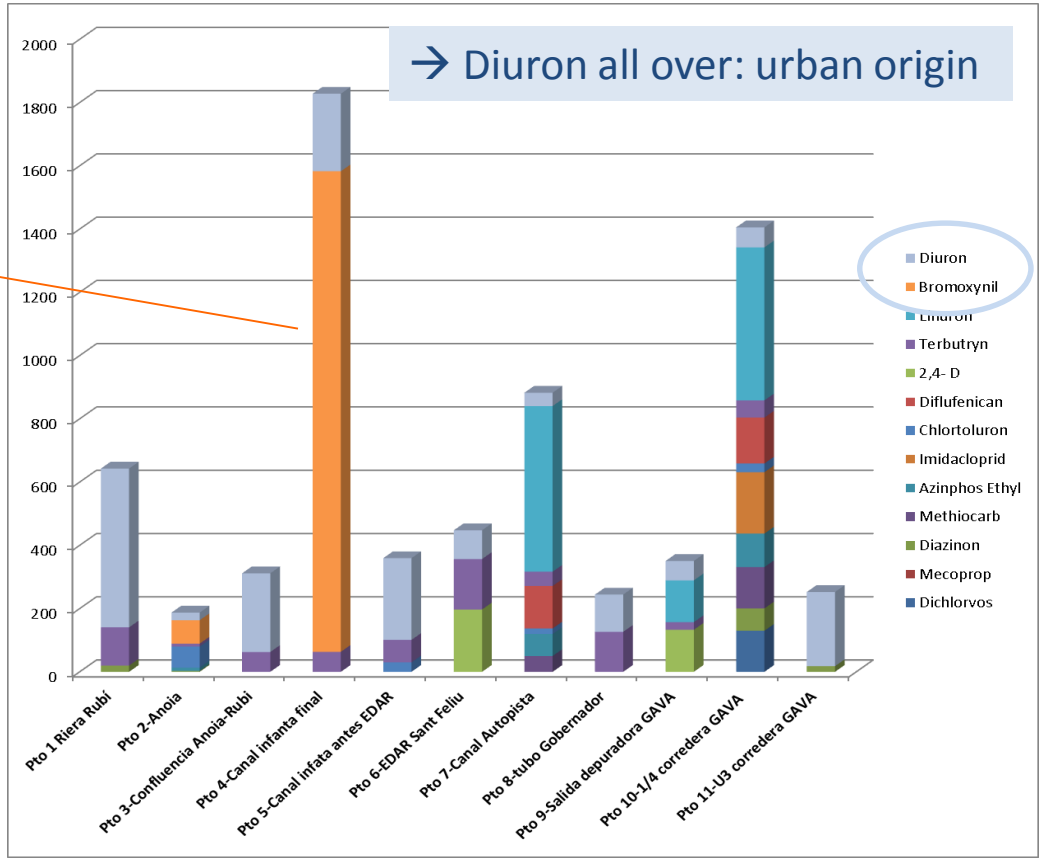
# ANALYSIS OF PESTICIDES IN WATER

First screening in 2017:
* 11 sites (surface water)
* 51 pesticides → 29 found




Cumulative levels of the most abundant compounds



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# TARGETED PESTICIDES (51)

WATERPROTECT

**Organ thiophosphates**

X Fenthion
Fenthion oxon
Fenthion sulfone
Fenthion sulfoxide
Fenthion oxon sulfone
Fenthion oxon sulfoxide

**Phenyl Ureas**

Linuron
Chlortoluron
Diuron*
Isoproturon*

**Triazines**

X Cyanazine
Desethylatrazine
Deisopropylatrazine
Terbutylazine
X Terbutryn
Cybutryn
X Simazine*
X Atrazine*

*Included in the **Directive 2013/39/EC** as PRIORITY SUBSTANCES.

**Organophosphates**

X Diazinon
Dimethoate
X Fenitrothion
Fenitrothion oxon
X Chlorfenvinphos
Chlorpyrifos
Malathion
Malaoxon
X Azinphos-Methyl
Azinphos-Methyl-Oxon
X Azinphos-Ethyl
X Dichlorvos

**Benzothiadiazines**

Bentazone**

**Acidic**

Mecoprop**
2,4 D
MCPA
Fluroxypyr

**Chloroacetanilides**

X Alachlor*
X Metolachlor

**Thiocarbamate**

X Molinate

**Anilide**

Propanil

**Other**

Bromoxynil
Diflufenican
Methiocarb
Oxyfluorfen
Thifensulfuron Methyl
Pendimethalin
Quinoxyfen

**Neonicotinoids**

Acetamiprid
Clothianidin
Imidacloprid
Thiacloprid
Thiamethoxam

# WATER QUALITY MONITORING PLAN

*Specific **monitoring plan** designed in the framework of WaterProtect:*

- ***Samples**: selected surface and ground waters:*
  - waters used for drinking water production as well as for industrial and agriculture use
  - irrigation and drainage waters
  - treated wastewater
  - monitoring wells
  - bypasses of polluted surface waters

- *Two different **periods** of the year (winter and summer)*

- ***Parameters**:*
  - *mineral characterization*
  - *108 pesticides,*
  - *stable isotopes of N, O, B (NO3, NH4).*

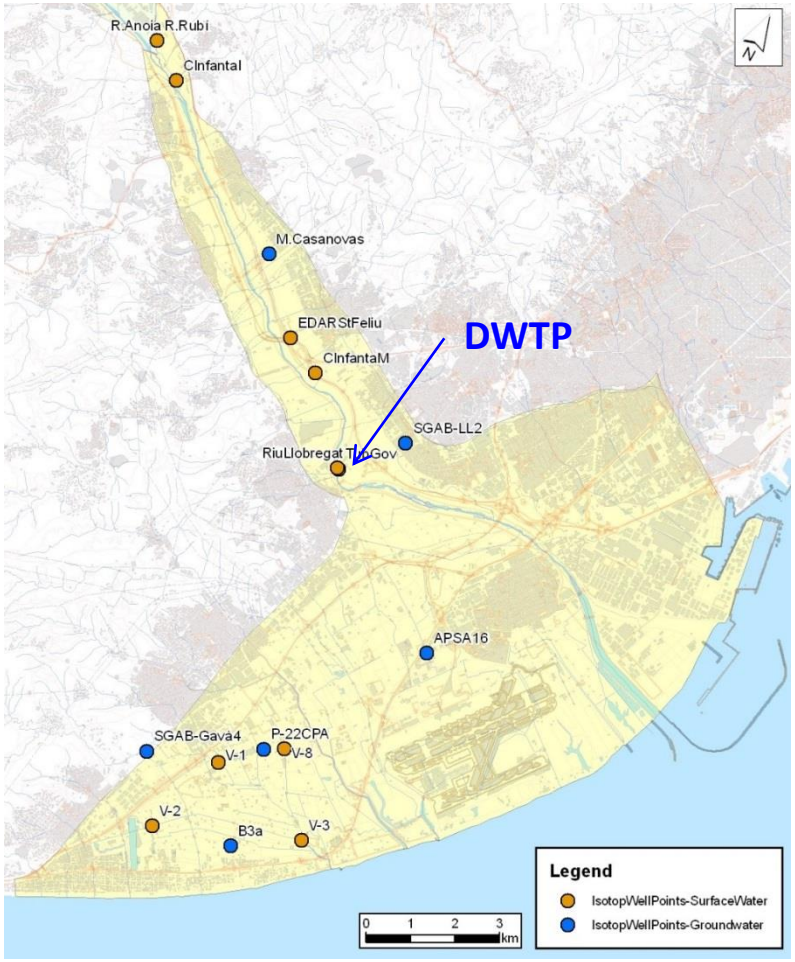


Fig.: Selected sampling sites (SWs and GWs)

*Quintana et al. Sci. Total Environ 692, 952-965, 2019.*



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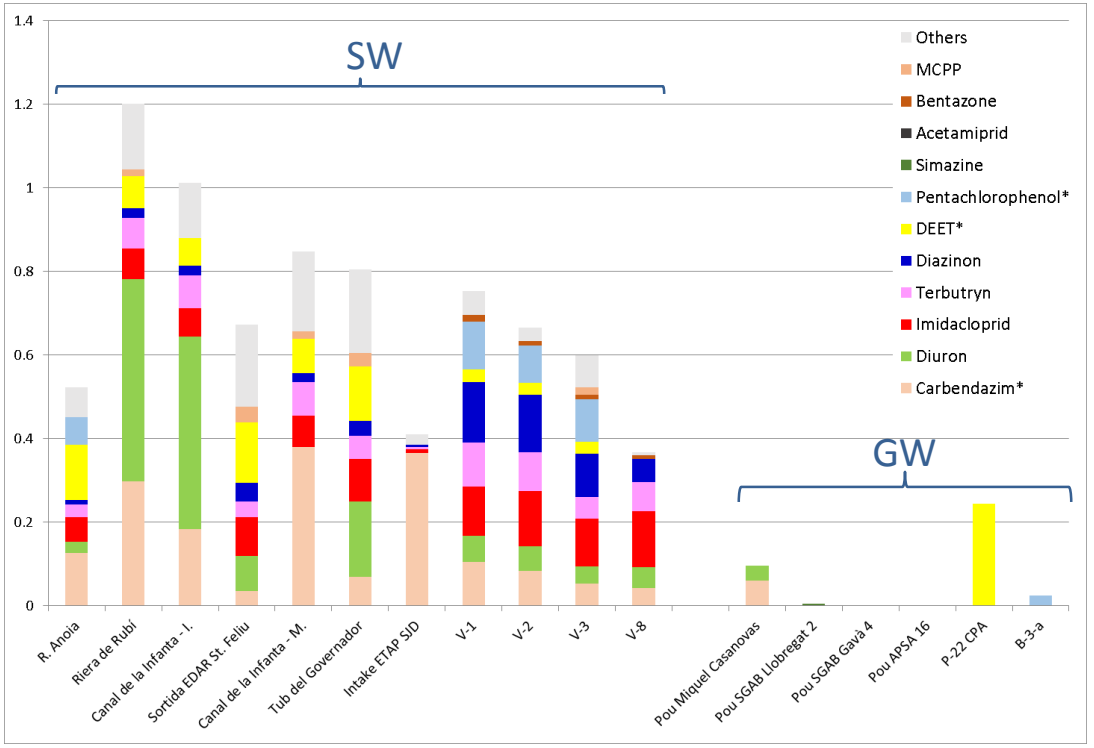
# PESTICIDES IN WATER – WINTER CAMPAIGN

- *22 (out of 108) pesticides found*
- *Most abundant and ubiquitous compounds in **surface waters (SW)**:*
  - ***Carbendazim** (Fung., 100%, sum 1.7 µg/L)*
  - ***Diuron** (Herb, 82%, 1.5 µg/L)*
  - ***Imidacloprid** (Inse., 100%, 1.0 µg/L)*
  - ***Terbutryn** (Herb, 100%, 0.7 µg/L)*
  - ***DEET** (Inse., 82%, 0.7 µg/L)*
  - ***Diazinon** (Inse., 100%, 0.6 µg/L)*
- *Widespread usage (crops diversity)*



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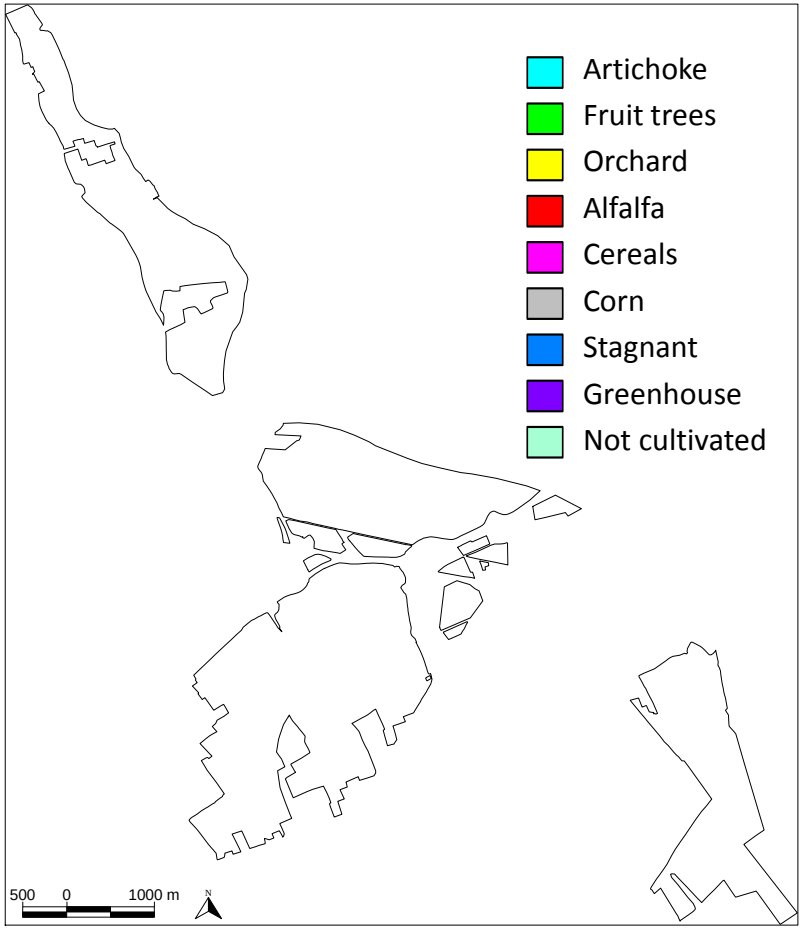
# AGRICULTURAL ACTIVITY




***Crops at the agrarian park***

*Main characteristics of the agricultural activity in the area:*

- *Agricultural tradition*
- *Typology and small size of farms*
- *Intensive production of orchards and fruit very varied*
- *Different production systems: conventional (GIP), eco, integrated*
- *The figure of the ADVs (for 30 years) (Agricultural advisers)*
- *Extensive or semi-ext. Livestock: sheep and chickens*
- *Different origins of irrigation water*
- *Different irrigation systems: gravity / pressure*



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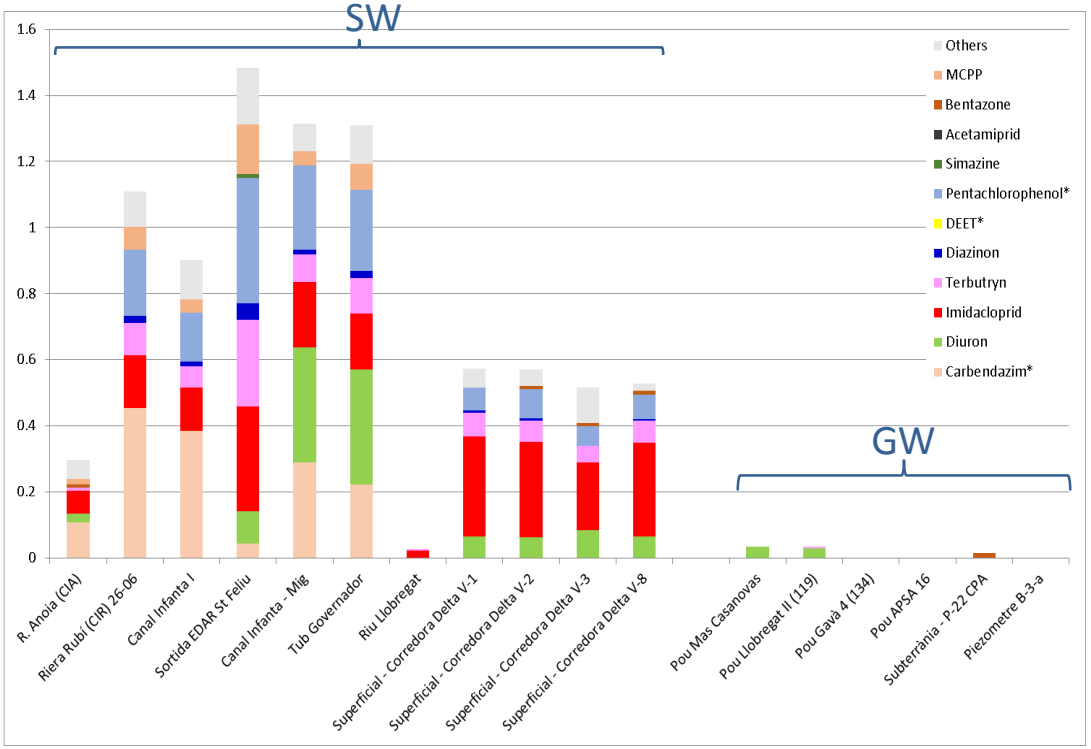
# PESTICIDES IN WATER – SUMMER CAMPAIGN

- *24 (out of 108) pesticides found*
- *Most abundant and ubiquitous compounds in **surface waters (SW)**:*

  - ***Carbendazim** (Fung., 55%, sum 1.5 µg/L)*
  - ***Diuron** (Herb, 73%, 1.8 µg/L)*
  - ***Imidacloprid** (Inse., 100%, 2.2 µg/L)*
  - ***Terbutryn** (Herb, 100%, 0.9 µg/L)*
  - ~~***DEET** (Inse., 82%, 0.7 µg/L)~~
  - ***Pentachlorofenol** ( 82%, 1.5 µg/L)*



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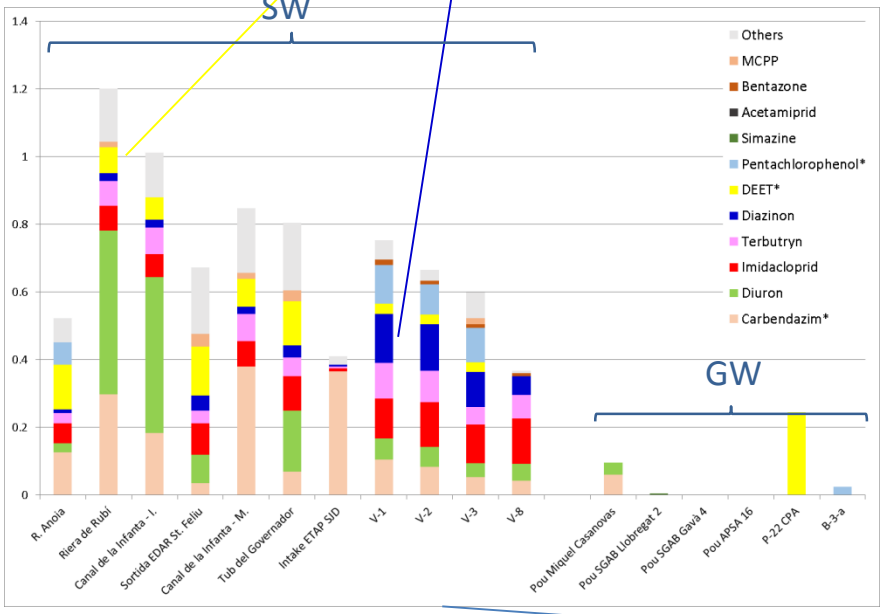
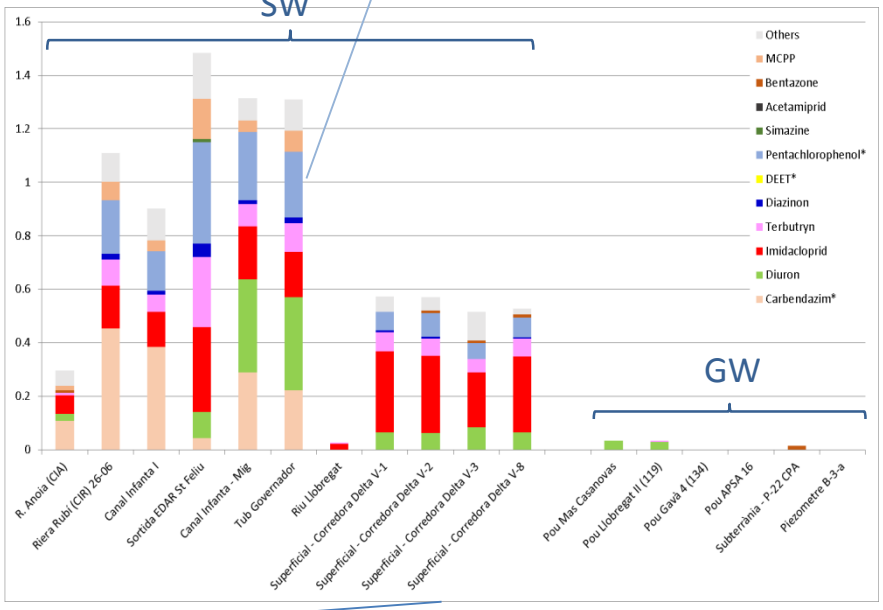
# PESTICIDES IN WATER – SEASONAL DIFFERENCES

*Stational differences (winter vs summer) → steady use of several pesticides along the year*

**DEET, diazinon**




**pentachorofenol**




*carbendazim, diuron, **imidacloprid,** terbutryn*



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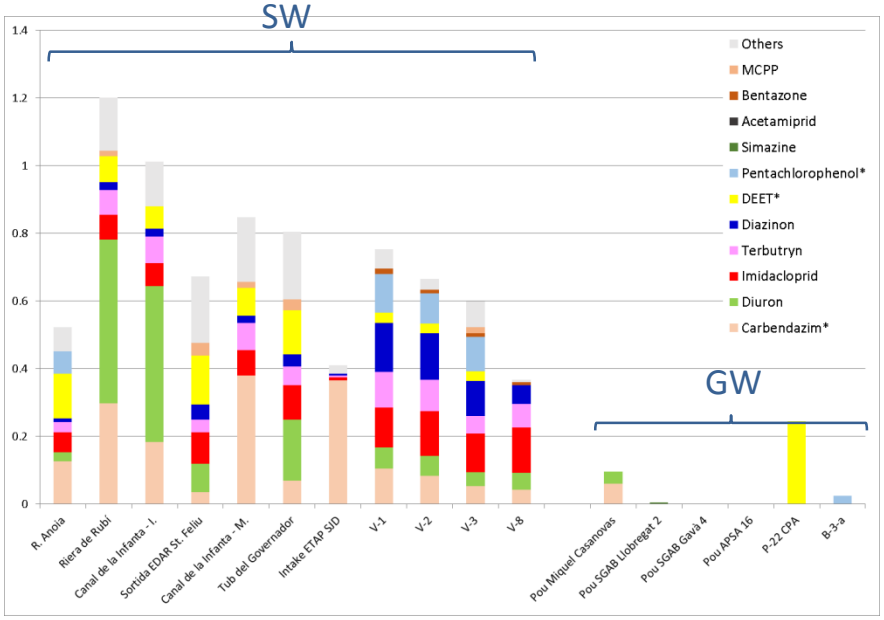
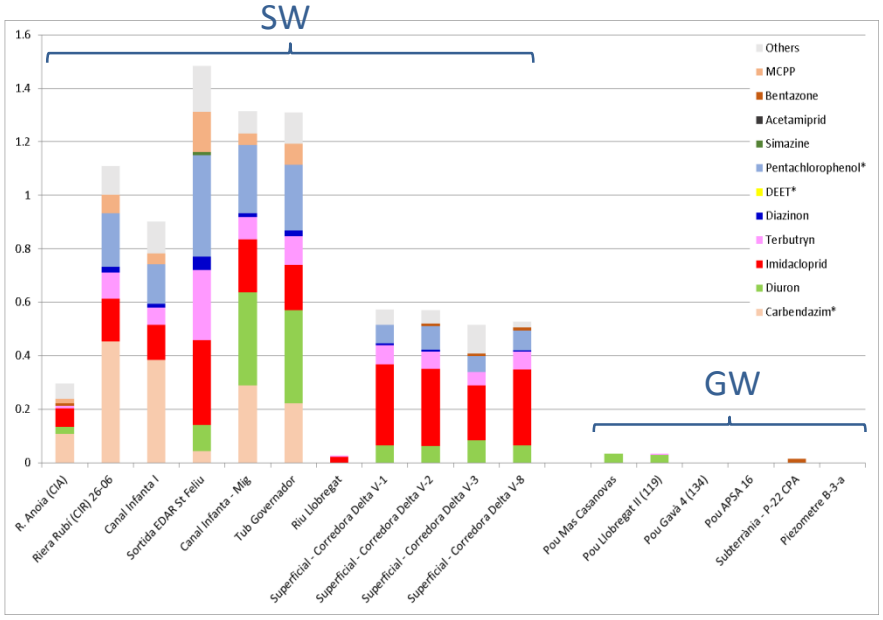
# PESTICIDES IN SURFACE WATERS – LEGISLATION (I)

*Compliance with **Directive 2013/39/EC** (**surface waters**): OK*

*All compounds < maximum admissible conc. (MAC)*

***diuron** & **terbutryn** > AA in 3 & 6 samples* - ***diuron** & **terbutryn** > AA in 2 & 9 samples*




AA: annual average



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# PESTICIDES IN SURFACE WATERS – LEGISLATION (II)

*Compliance with **Directive 2013/39/EC** (**surface waters**): OK*

*→ diuron & terbutryn > annual average (AA) , < maximum admissible conc. (MAC)*

*Compliance with **RD 817/2015***
***Specific pollutants** (sustancias preferentes ): OK*

| Nº | Nº CAS(1) | Nombre de la sustancia | NCA-MA(2) Aguas superficiales continentales (3) | | NCA-MA (2) Otras aguas superficiales |
|---|---|---|---|---|---|
| (1) | 100-41-4 | Etilbenceno | 30 | | 30 |
| (2) | 108-88-3 | Tolueno | 50 | | 50 |
| (3) | 71-55-6 | 1, 1, 1 – Tricloroetano | 100 | | 100 |
| (4) | 1330-20-7 | Xileno (Σ isómeros orto, meta y para) | 30 | | 30 |
| (5) | 5915-41-3 | Terbutilazina | 1 | | 1 |
| (6) | 7440-38-2 | Arsénico | 50 | | 25 |
| (7) | 7440-50-8 | Cobre (4) | Dureza del agua (mg/L $CaCO_3$)<br>$CaCO_3 \leq 10$<br>$10 < CaCO_3 \leq 50$<br>$50 < CaCO_3 \leq 100$<br>$CaCO_3 > 100$ | NCA-MA<br>5<br>22<br>40<br>120 | 25 |
| (8) | 18540-29-9 | Cromo VI | 5 | | 5 |
| (9) | 7440-47-3 | Cromo | 50 | | no aplicable |
| (10) | 7782-49-2 | Selenio | 1 | | 10 |
| (11) | 7440-66-6 | Zinc(4) | Dureza del agua (mg/L $CaCO_3$)<br>$CaCO_3 \leq 10$<br>$10 < CaCO_3 \leq 50$<br>$50 < CaCO_3 \leq 100$<br>$CaCO_3 > 100$ | NCA-MA<br>30<br>200<br>300<br>500 | 60 |
| (12) | 74-90-8 | Cianuros totales | 40 | | no aplicable |
| (13) | 16984-48-8 | Fluoruros | 1700 | | no aplicable |
| (14) | 108-90-7 | Clorobenceno | 20 | | no aplicable |
| (15) | 25321-22-6 | Diclorobenceno (Σ isómeros orto, meta y para) | 20 | | no aplicable |
| (16) | 51218-45-2 | Metolacloro | 1 | | no aplicable |



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# PESTICIDES IN SURFACE WATERS – LEGISLATION (III)

*Compliance with **Directive 2013/39/EC (surface waters)**: OK*

*→ diuron & terbutryn > annual average (AA) , < maximum admissible conc. (MAC)*

*Compliance with **RD 817/2015 Specific pollutants** (sustancias preferentes ): OK*

*Compliance with **Watch List (2018/840)**: OK*

Imidacloprid
(all samples in C1)

Acetamiprid
(4 samples in C2)

**Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC**

| Name of substance/group of substances | CAS number (1) | EU number (2) | Indicative analytical method (3) (4) (5) | Maximum acceptable method detection limit (ng/l) |
|---|---|---|---|---|
| 17-Alpha-ethinylestradiol (EE2) | 57-63-6 | 200-342-2 | Large-volume SPE — LC-MS-MS | 0,035 |
| 17-Beta-estradiol (E2), Estrone (E1) | 50-28-2, 53-16-7 | 200-023-8 | SPE — LC-MS-MS | 0,4 |
| Diclofenac | 15307-86-5 | 239-348-5 | SPE — LC-MS-MS | 10 |
| 2,6-Ditert-butyl-4-methylphenol | 128-37-0 | 204-881-4 | SPE — GC-MS | 3 160 |
| 2-Ethylhexyl 4-methoxycinnamate | 5466-77-3 | 226-775-7 | SPE — LC-MS-MS or GC-MS | 6 000 |
| Macrolide antibiotics (6) | | | SPE — LC-MS-MS | 90 |
| Methiocarb | 2032-65-7 | 217-991-2 | SPE — LC-MS-MS or GC-MS | 10 |
| Neonicotinoids (7) | | | SPE — LC-MS-MS | 9 |
| Oxadiazon | 19666-30-9 | 243-215-7 | LLE/SPE — GC-MS | 88 |
| Tri-allate | 2303-17-5 | 218-962-7 | LLE/SPE — GC-MS or LC-MS-MS | 670 |



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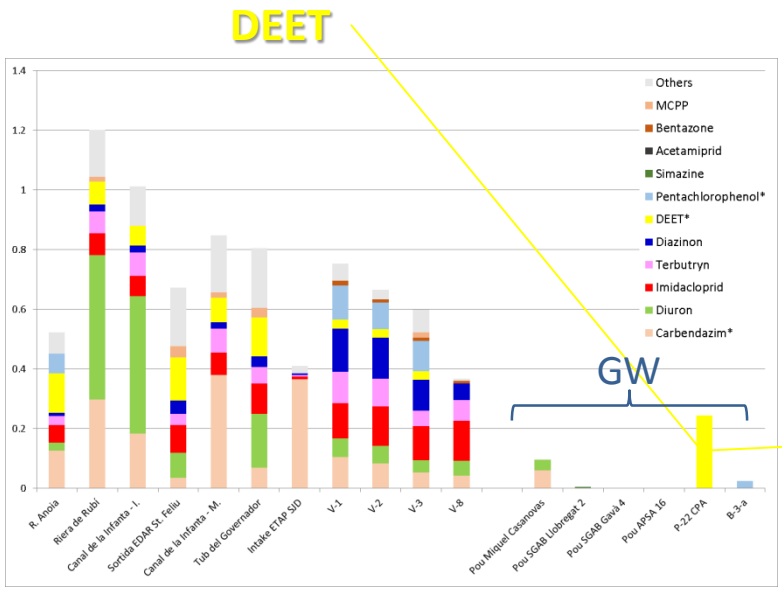
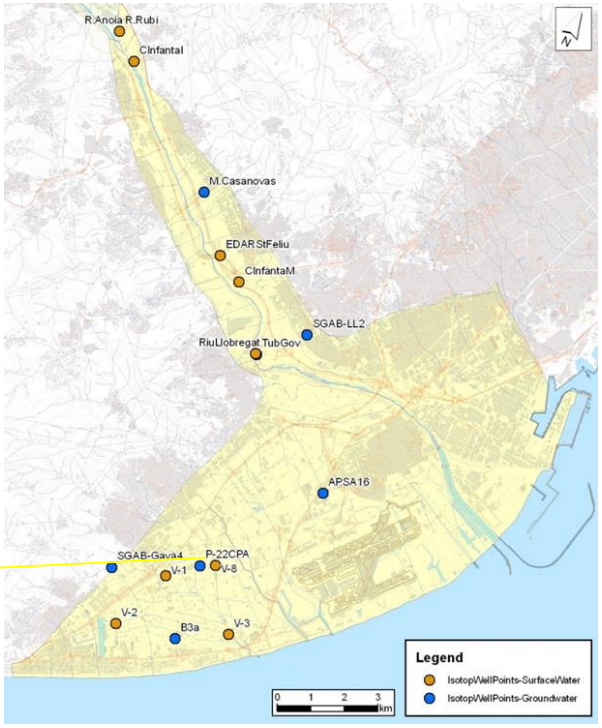
# PESTICIDES IN GROUNDWATER – LEGISLATION

- *Only 7 compounds found: bentazone, carbendazim, DEET, diuron, pentachlorophenol, simazine, and terbutryn.*
- *Simazine: only compound found in GW and not in SW (old pollution)*
- *Compliance with **Directive 2006/118/EC** (groundwaters): 1 single exceedance (DEET>100 ng/L in winter in P-22CPA, a well located in an agricultural area under the influence of both surface water recharge and direct land*



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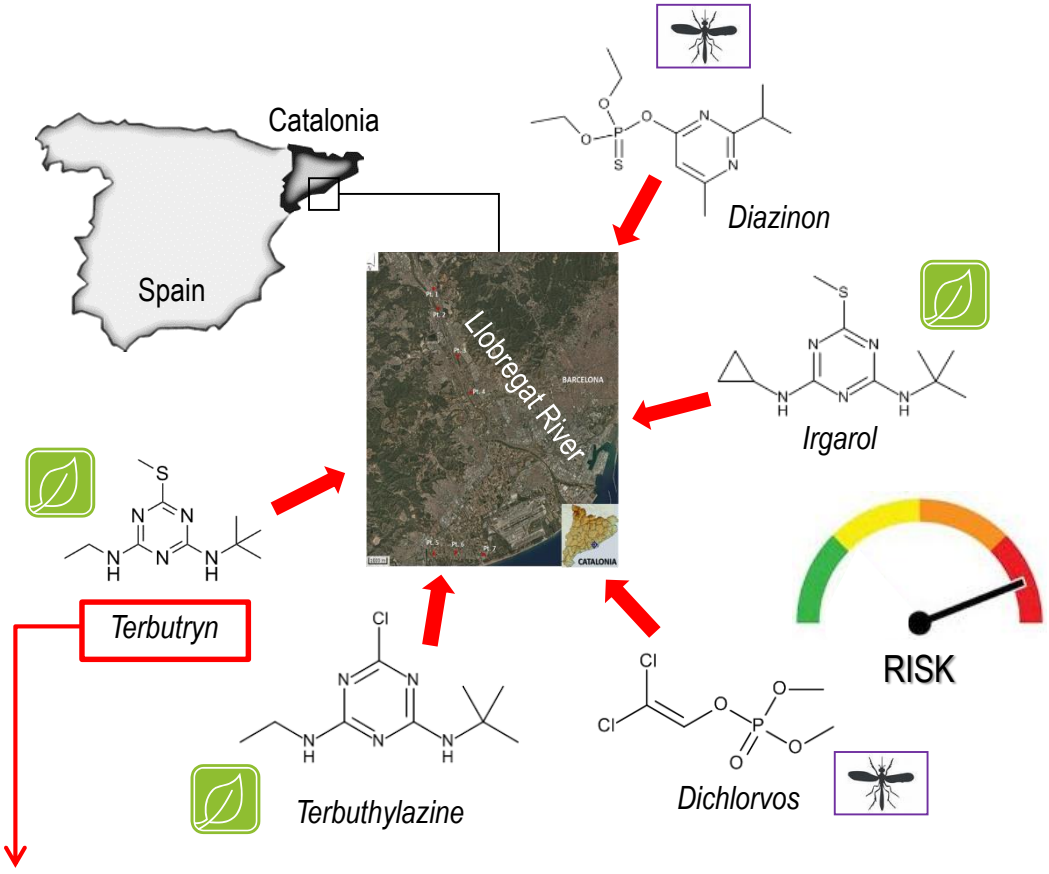
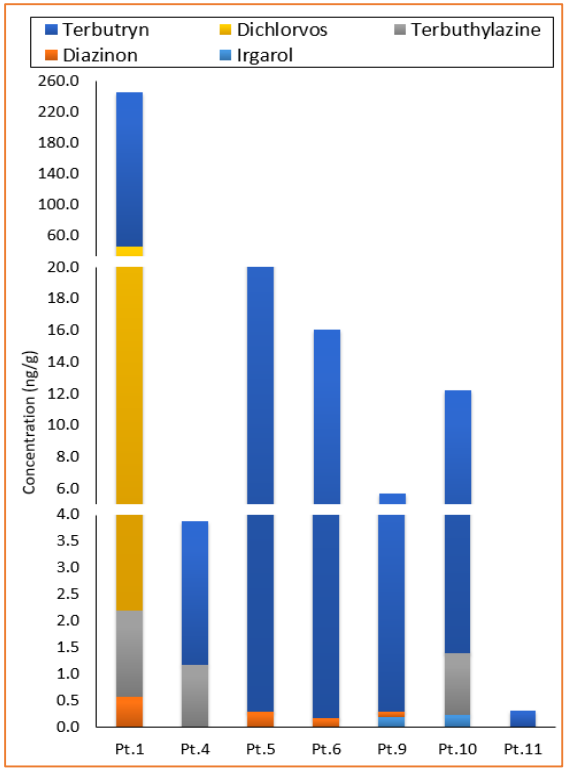
# PESTICIDES IN SEDIMENTS




5 out of 50 comp. investigated




Most ubiquitous and abundant, ↑ conc. (up to 200 ng/g)
Control agent for grasses and broadleaf weeds in various cultivations (e.g., wheat, barley, sunflower, potatoes) and aquatic herbicide for the control of algae in water courses, reservoirs, and fish ponds.
Priority substance in water (EQS = 34 ng/L) (up to 200 ng/g)

*Barbieri et al. Anal. Bioanal. Chem. (in press)*



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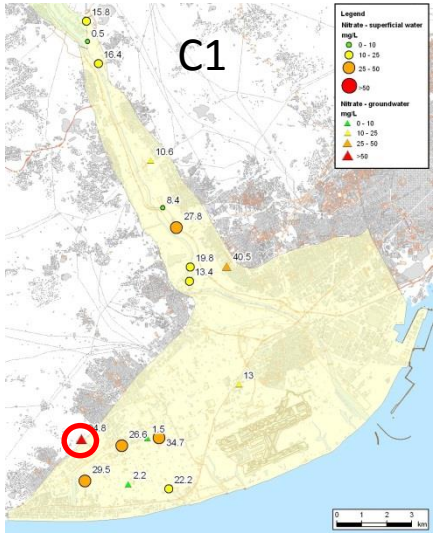
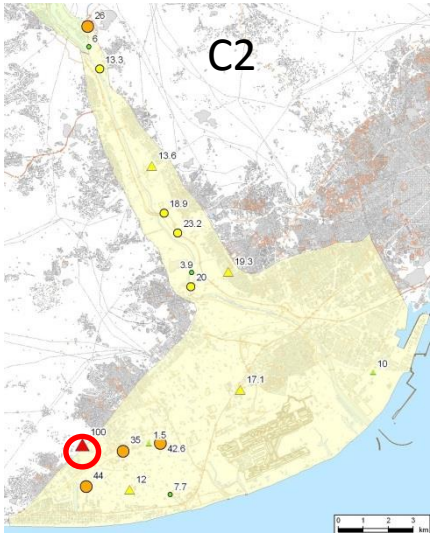
# ISOTOPES

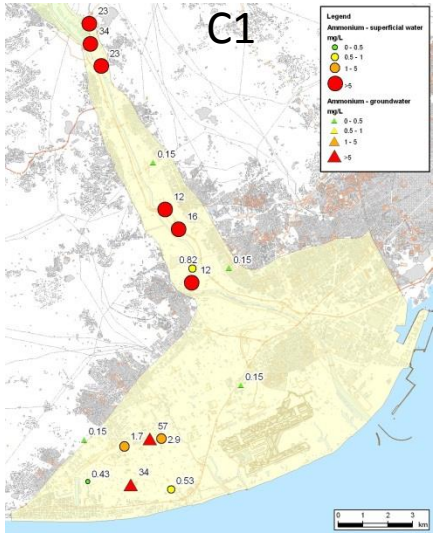


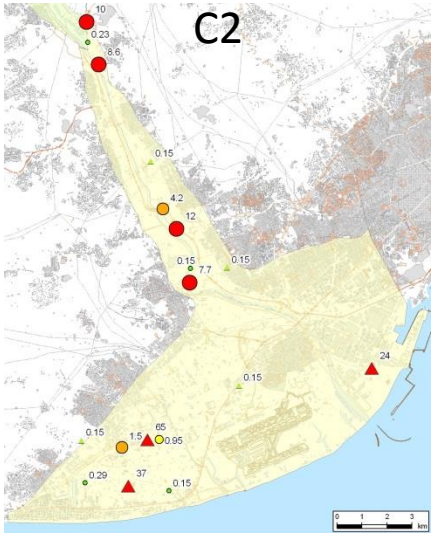

**Pollution by**

Nitrates: > 50 mg/L

Ammonium: > 0.5 mg/L



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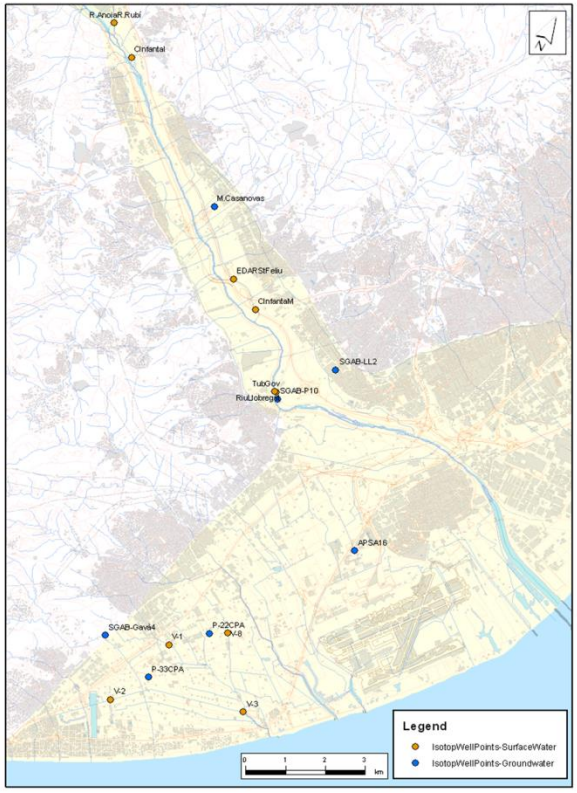
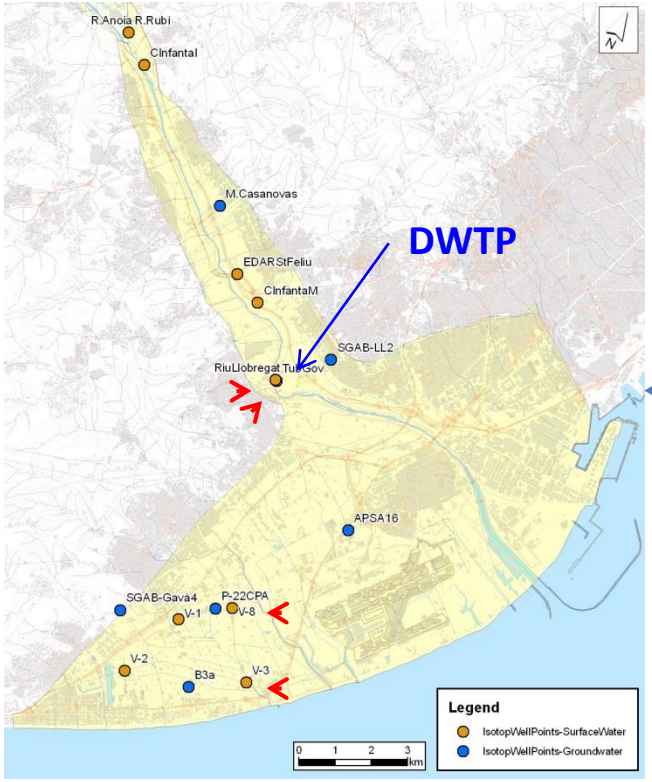
# ISOTOPES

Two campaigns:

January 2019 – 17 samples (6 GW, 10 SW, 1 WW) – $\delta^{15}$N-$NO_3^-$ and $\delta^{18}$O-$NO_3^-$ isotopes

June 2019 – 12 samples – $\delta^{15}$N-$NO_3^-$, $\delta^{18}$O-$NO_3^-$, $\delta^{15}$N-$NH_4^+$ (9 samples), $\delta^{11}$B isotopes (4 s.)



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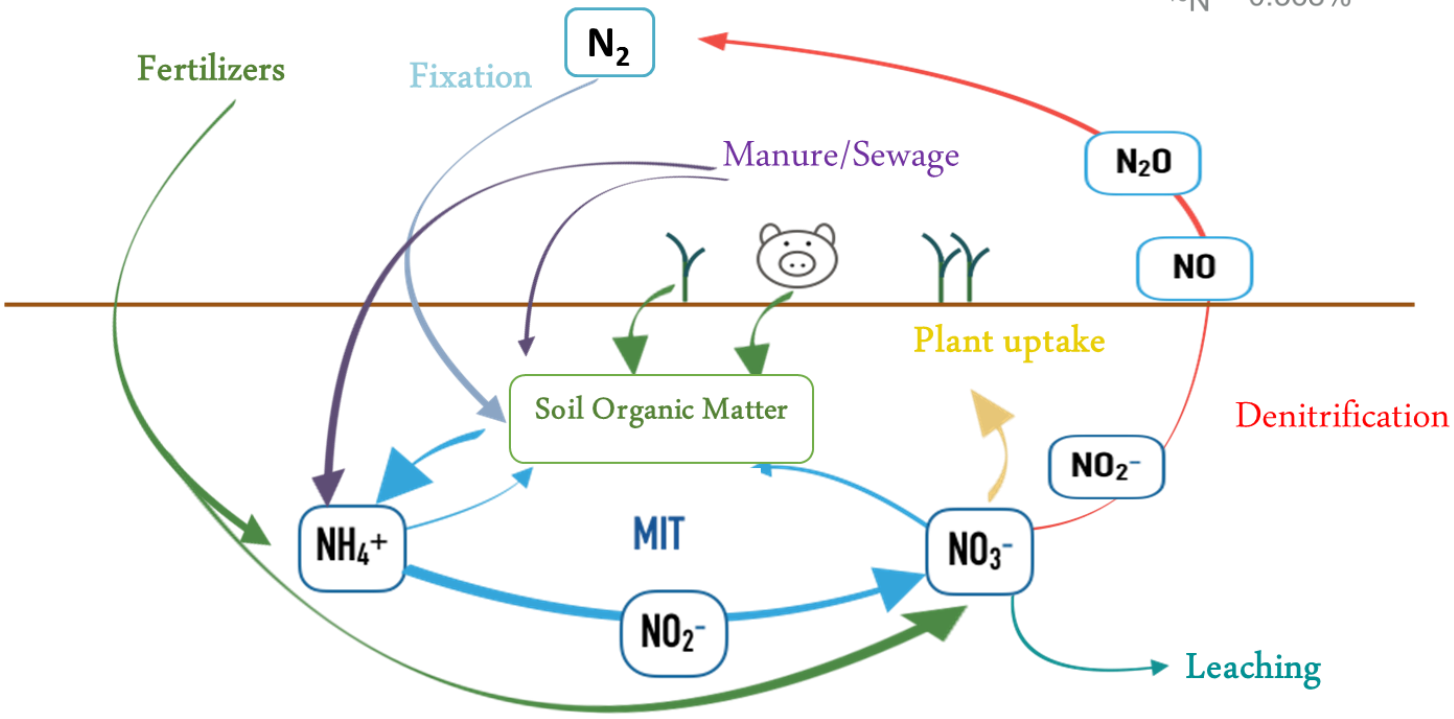
## Why isotopes provide info on the source of the N compounds?

Same atomic number and different mass number.

| | | | |
|---|---|---|---|
| $^{14}N$ | 99.632% | $^{16}O$ | 99.757 % |
| $^{15}N$ | 0.368% | $^{17}O$ | 0.038 % |
| | | $^{18}O$ | 0.205 % |



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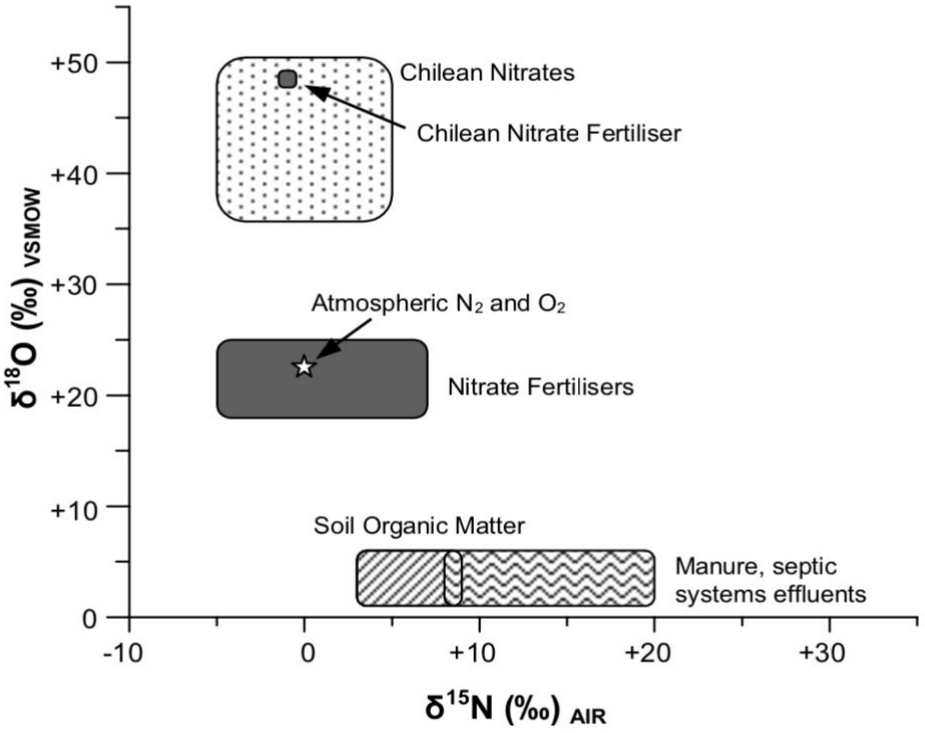
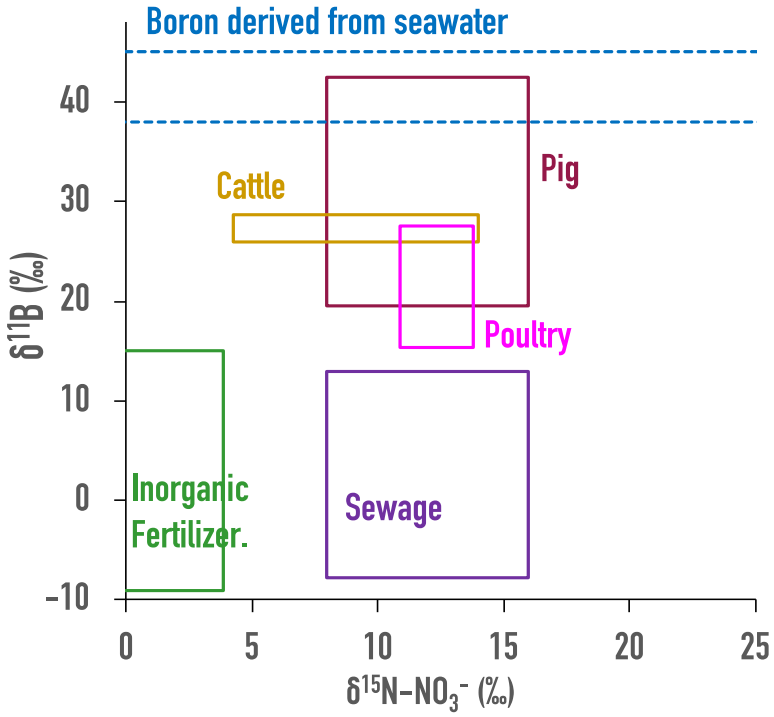
# ISOTOPES

## Different N, O isotopic composition depending on the source

→ Isotopes of boron to distinguish between manure and sewage



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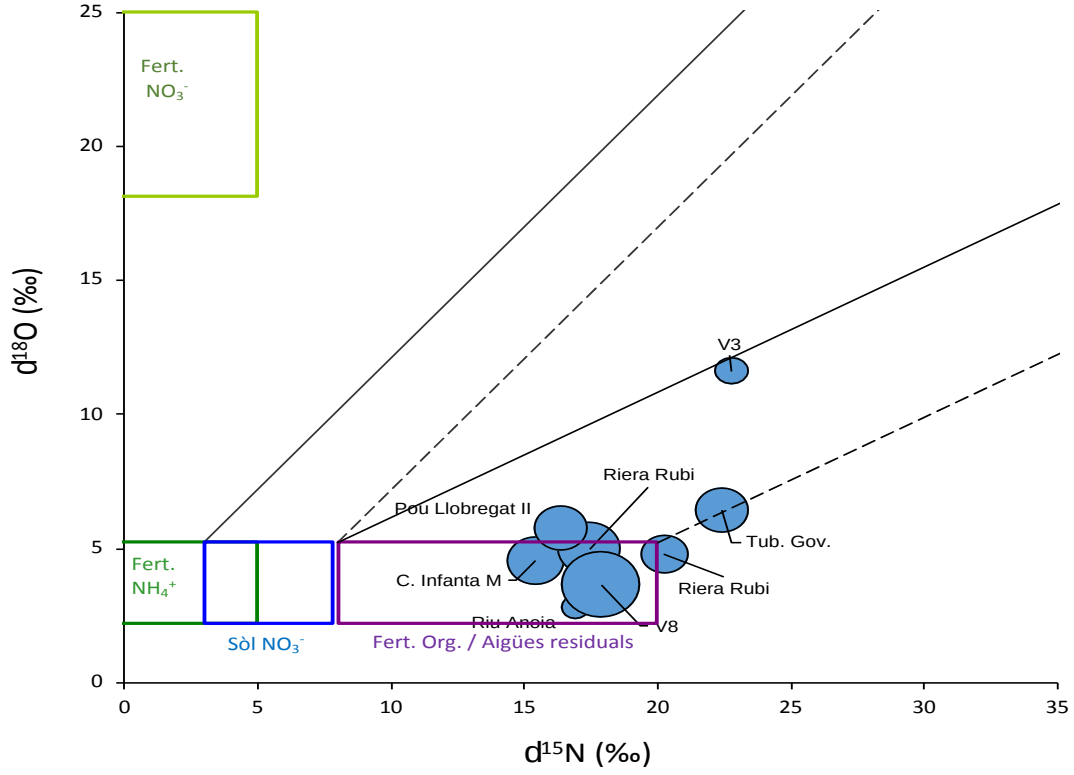
## Results second sampling campaign




Organic source



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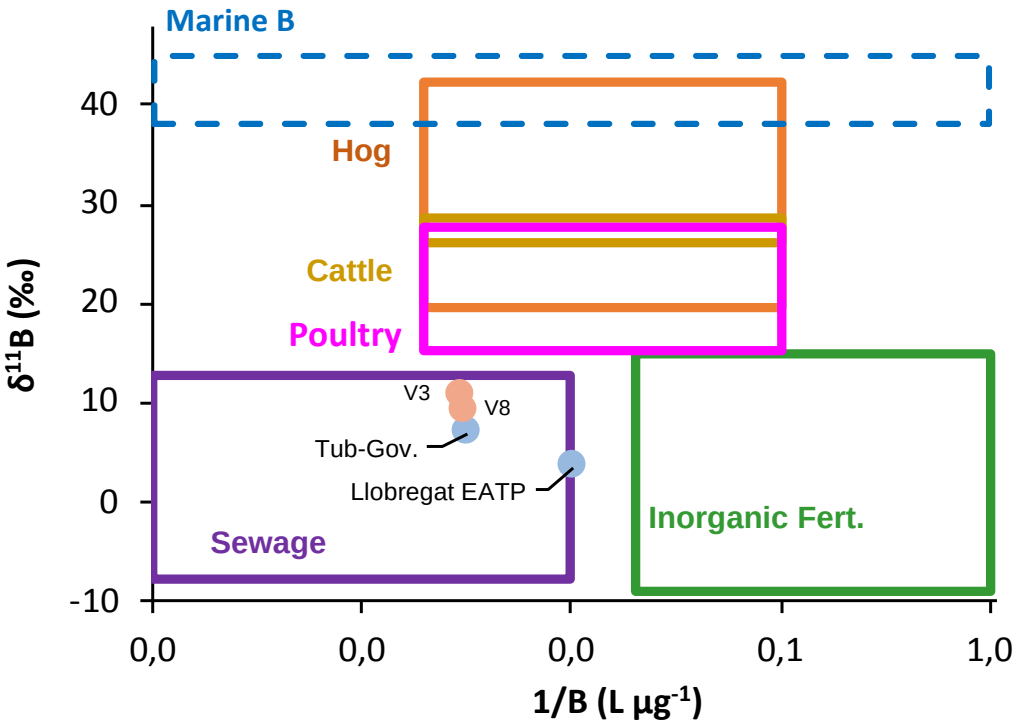
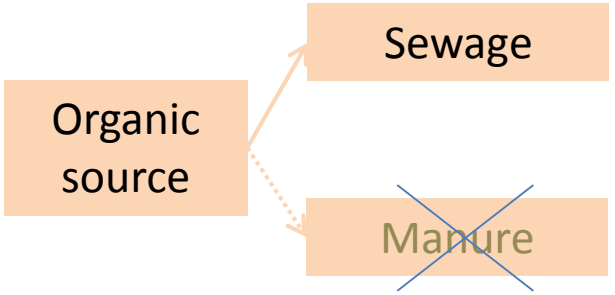
## Results second sampling campaign



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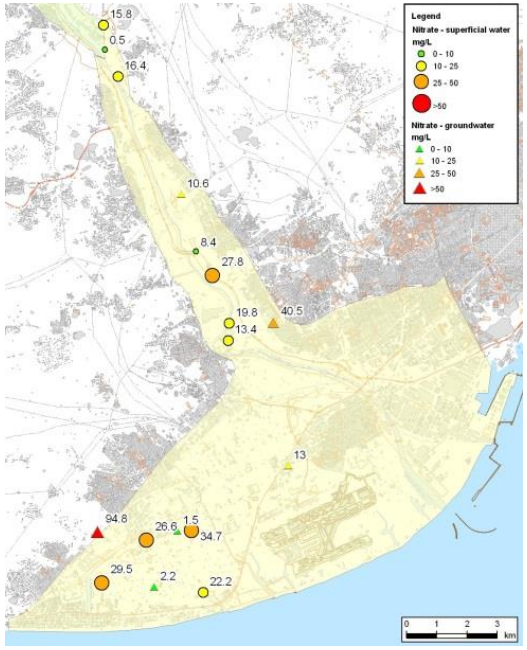
# ISOTOPES

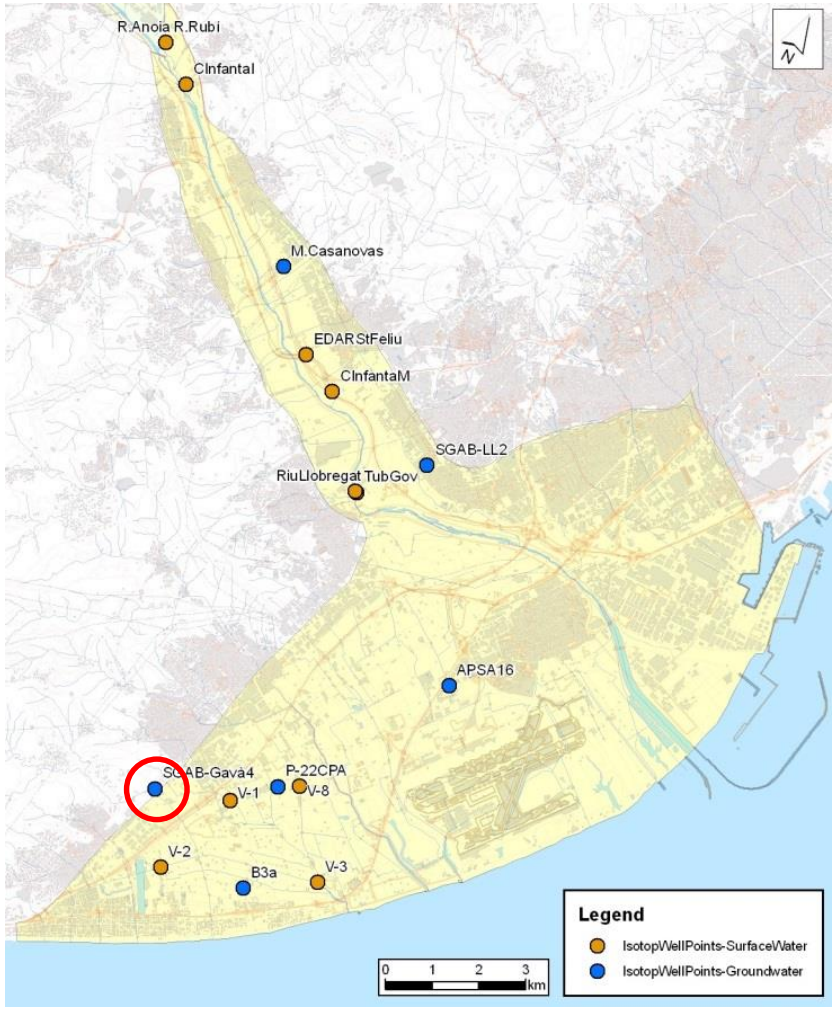
## General contamination by nitrates and ammonium of sewage origen




**exception :**

inorganic fertilizers

Nitrates > 50 mg/L



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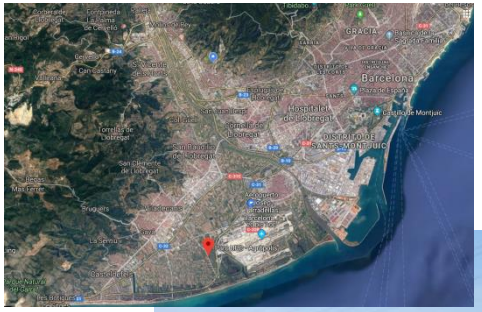
# WP3&4 - PARTICIPATORY MONITOR. & BMP

***Evaluation of in-situ biorremediation techniques for water contaminated with pesticides***




Agrópolis location

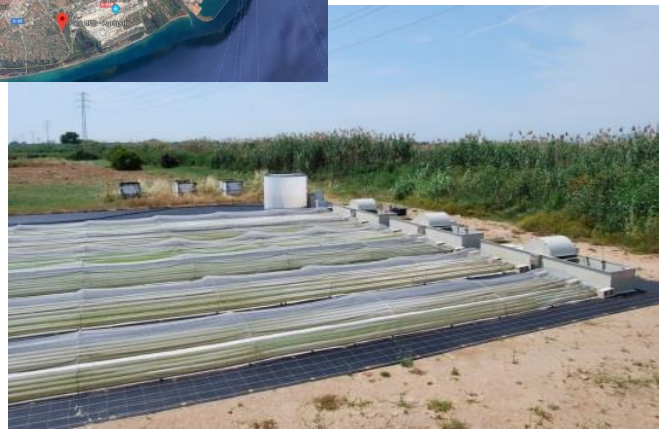


*Fig. Tubular Horizontal Photobioreactor used in the experiments*

**Objective**: evaluate the efficiency of a newly designed full-scale Hybrid Tubular Horizontal Photobioreactor (HTH-PBR) to treat agricultural runoff water in a demonstrative plant (Agrópolis) that the UPC has in the Baix Llobregat rural area.

**Collaboration** with the Polytechnic University of Catalonia (UPC), in the frame of the H2020 project INCOVER (Innovative Eco-Technologies for Resource Recovery from Wastewater)

**Methodology**: samples of the inlet (mix of agricultural and urban wastewater) and outlet of the PBR were collected three days per week during two consecutive weeks and analysed for a total of 50 pesticides, including metabolites, belonging to different classes.



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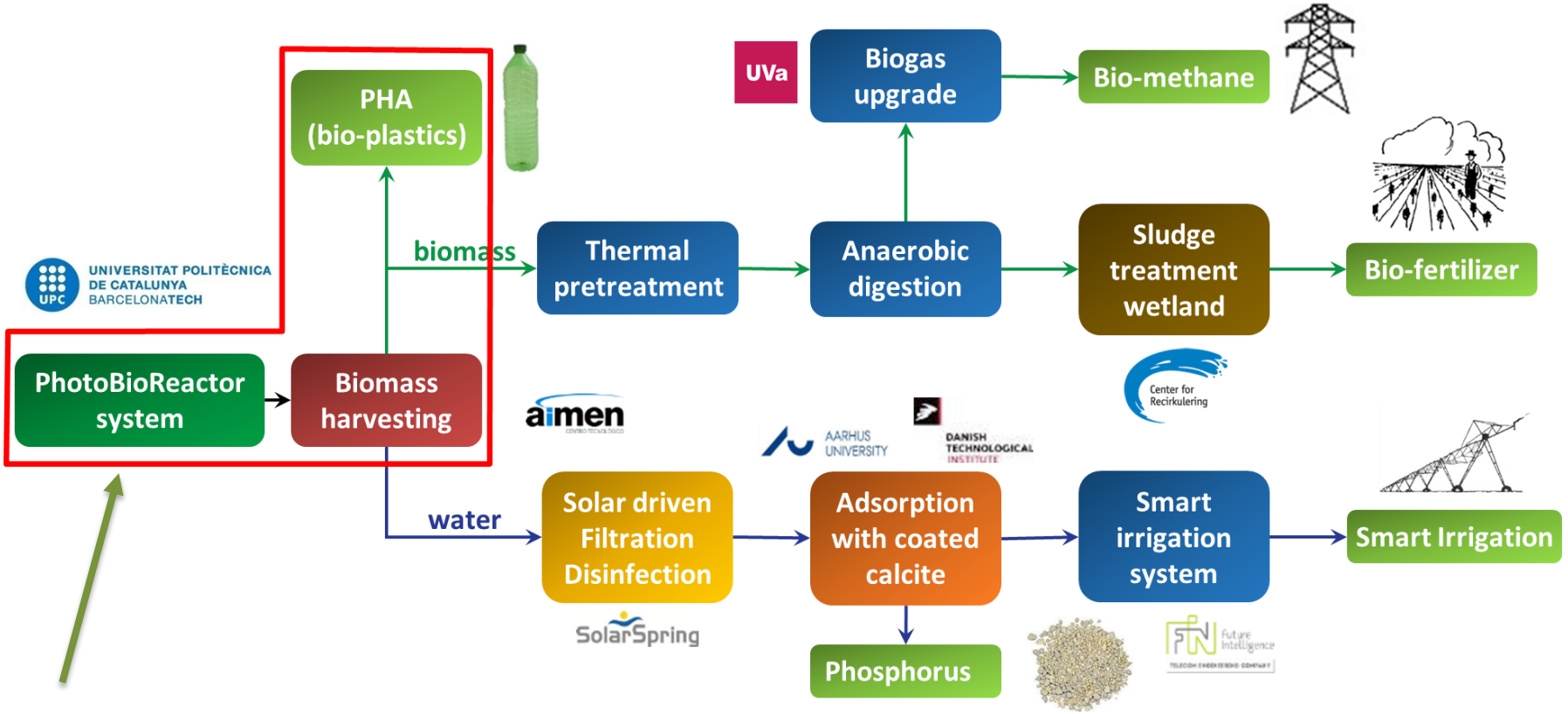
# SINERGIES WITH OTHER PROJECTS - INCOVER

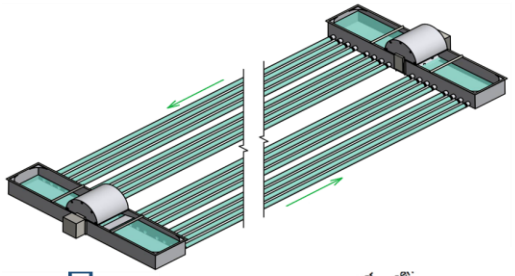
*Evaluation of in-situ biorremediation techniques for agricultural drainage water*
*Overall objective of the PBR → generation of **profitable bioproducts** from wastewater and microalgae biomass (circular economy and biorefinery).*




**H2020- INCOVER:** Innovative Eco-Technologies for Resource Recovery from Wastewater (06-2016/07-2019)

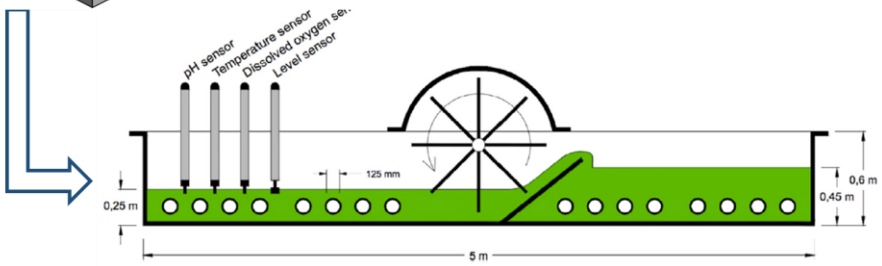
# SINERGIES WITH OTHER PROJECTS - INCOVER

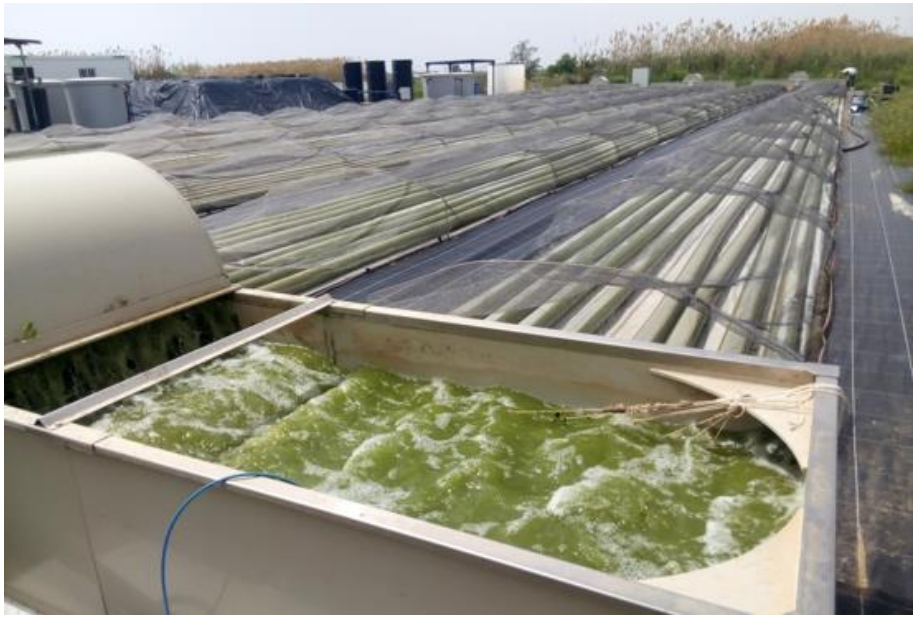
## Tubular horizontal semi-closed PBR



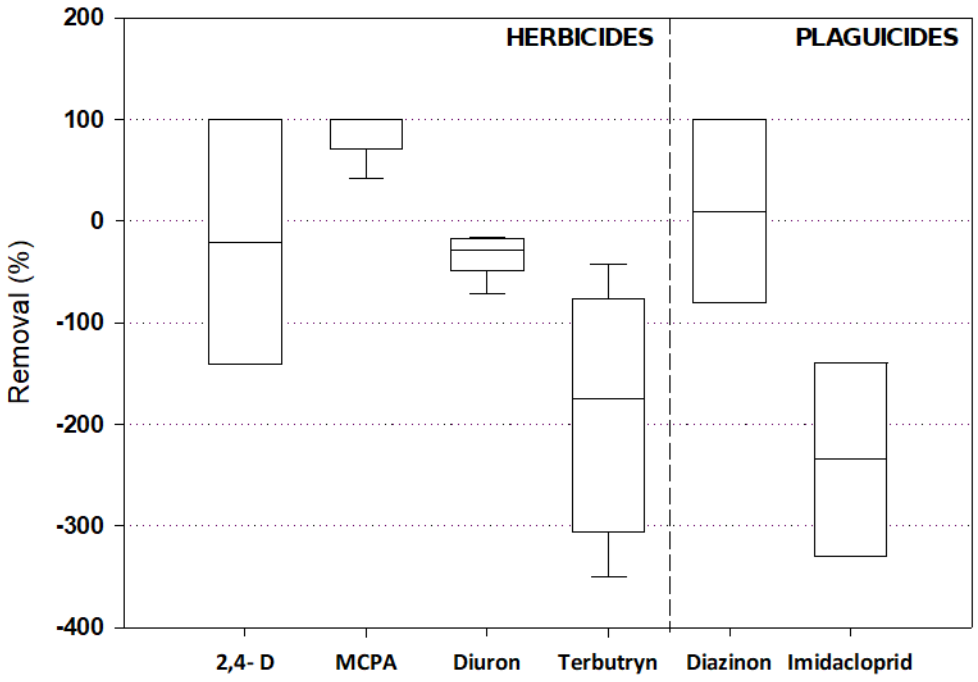
| Parameter | Value |
|---|---|
| Total volume ($m^3$) | 11.7 |
| Tube diameter (mm) | 125 |
| Tube length (m) | 47 |
| Number of tubes | 16 |
| Engine power (kW) | 0.25 |
| HRT (d) | 5 |

Uggetti et al. (2018) Water Sci Technol **78**(1-2), 114-124.
García et al. (2018) Ecol Eng **120**, 513-521.



# SINERGIES WITH OTHER PROJECTS - INCOVER




- ✓ A total of **51 pesticides**, including 10 of their main transformation products, were studied.
- ✓ **16** were detected in the agricultural runoff.
  - 100 % removal for **10** of them
  - MCPA was removed in a 88.5% (average)
  - Negative eliminations for diuron, terbutryn and imidacloprid
  - Variable eliminations, ranging from negative to 100%, for 2,4-D and diazinon

- ✓ Treatment considered one the most environmentally favorable and less expensive (reduced energy requirements and zero chemical inputs)→ further investigation for optimum operational conditions.
- ✓ Submission for publication in the **Special Issue**.



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# CONCLUSIONS

- ✓ ***Four compounds*** *dominate the spectrum of pesticide pollution in the area: Carbendazim, Diuron, Imidacloprid, and Terbutryn.*
- ✓ *Their* ***origin*** *is difficult to know but many of them show widespread urban use.*
- ✓ *Diuron, terbutryn, imidacloprid, acetamiprid and DEET in waters, and terbutryn, dichlorvos, irgarol, diazinon, and terbuthylazine in sediments require* ***further investigation****.*
- ✓ *Pollution by* ***nitrates*** *is in general associated to sewage, rather synthetic or organic fertilizers.*
- ✓ *To ensure safe drinking water, especially in drought periods, measures adopted to* ***substitute and reduce the use of pesticides*** *will aid in controlling pollutants from urban, industrial and agricultural origin.*
- ✓ ***Algae-based bio-remediation*** *techniques have shown variable removal efficiencies depending on the pesticide.*



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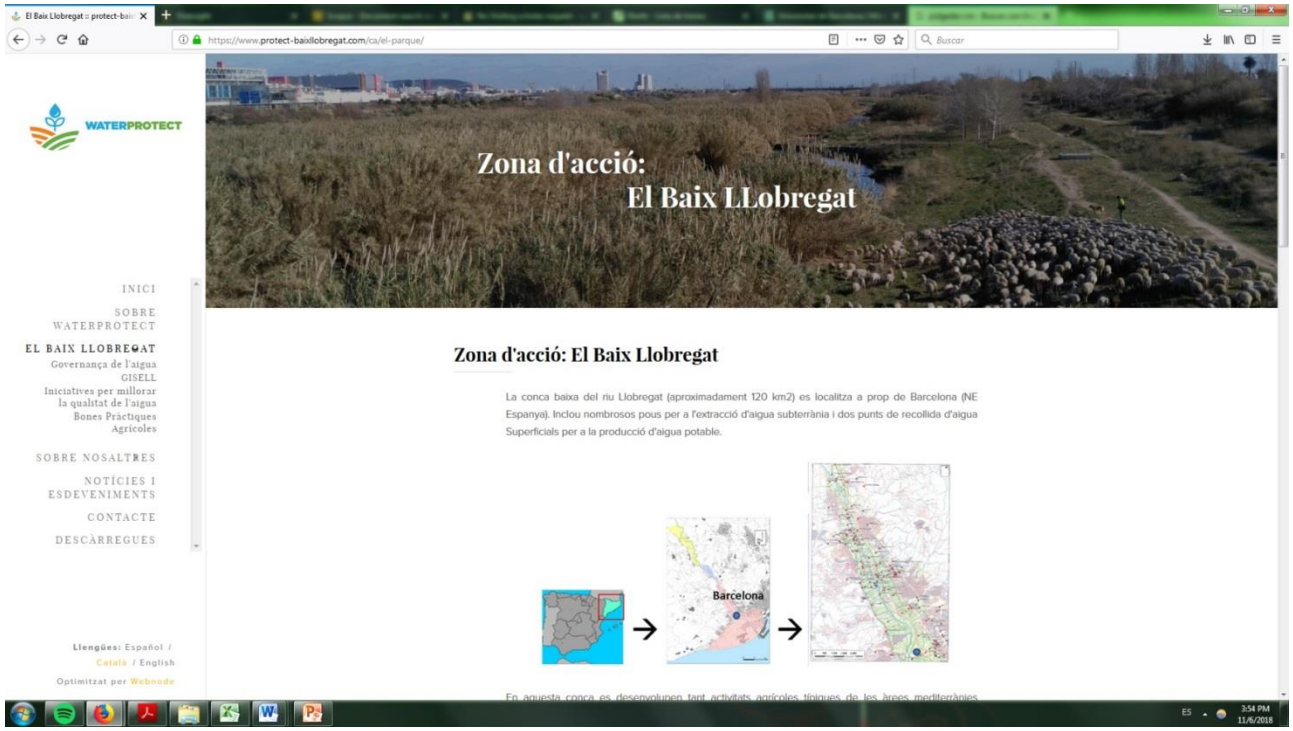
# MORE INFORMATION

Webpage of the Spanish action lab in Catalan/Spanish and English.




https://www.protect-baixllobregat.com/ca/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WATERPROTECT


CSIC
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UPC
Universitat Politècnica de Catalunya
BarcelonaTech
Group of Environmental Engineering and Microbiology



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