



LE STUDIUM CONFERENCES

MICROPOLLUTANTS IN
GROUNDWATER : FROM
RESEARCH STUDIES TO
REGULATION

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Water micropollutants: from detection to removal
Orléans 26-28 November 2018



Micropollutants in Groundwater: from research studies to regulation

> **Setting the scene:**

- What is a micropollutant? What are emerging compounds?
- Different types and sources of pollutants
- Issues regarding micropollutants in groundwater resources

> **Prioritisation of micropollutants in French groundwater**

- Prioritisation: a part of the solution
- Why and how to prioritise chemicals?
- European initiatives

> **Prospective and regulatory surveillance of micropollutants in groundwater**

- The first “exceptional campaign in 2011-2012”
- State of the knowledge
- Future surveillance



SETTING THE SCENE

General definitions

> **Pollutant = molecule whose presence in the environment causes problems**

- Persistent and / or huge and continuous emission
- Toxic for humans and / or ecotoxic for environment
- May cause adverse effect in humans or ecosystems
- Limit one or several use of water, soil



> **Micropollutants = molecule whose concentration is very weak in water, soil or air**

- Microgramme or nanogramme per litre (grain of sugar in an Olympic swimming pool)
- Detection in natural water depends on analytical performances

Different types of micropollutants – chemical family

> Inorganic pollutants

- 1. heavy metals

⇒ Main: **Cd, Cr, Cu (copper), Hg (mercury), Ni, Pb (lead), Zn**

- 2. Non-Metalloids

⇒ Main: **As, Se, ...**

« natural » pollutants
(non synthetic)

Mining, industrials...

1 H 1,008																	2 He 4,00						
3 Li 6,94	4 Be 9,01											5 B 10,81	6 C 12,01	7 N 14,01	8 O 16,00	9 F 19,00	10 Ne 20,18						
11 Na 23,00	12 Mg 24,31											48 Cd 112,40						13 Al 26,98	14 Si 28,09	15 P 30,97	16 S 32,06	17 Cl 35,45	18 Ar 39,95
19 K 39,10	20 Ca 40,08	21 Sc 44,96	22 Ti 47,90	23 V 50,94	24 Cr 52,00	25 Mn 54,94	26 Fe 55,85	27 Co 58,93	28 Ni 58,71	29 Cu 63,55	30 Zn 65,38	31 Ga 69,72	32 Ge 72,59	33 As 74,92	34 Se 78,96	35 Br 79,90	36 Kr 83,80						
37 Rb 85,47	38 Sr 87,62	39 Y 88,91	40 Zr 91,22	41 Nb 92,91	42 Mo 95,94	43 Tc 98,91	44 Ru 101,07	45 Rh 102,90	46 Pd 106,40	47 Ag 107,90	48 Cd 112,40	49 In 114,80	50 Sn 118,70	51 Sb 121,80	52 Te 127,60	53 I 126,90	54 Xe 131,30						
55 Cs 132,90	56 Ba 137,30	57 La* 138,90	72 Hf 178,50	73 Ta 181,00	74 W 183,90	75 Re 186,20	76 Os 190,20	77 Ir 192,20	78 Pt 195,10	79 Au 197,00	80 Hg 200,60	81 Tl 204,40	82 Pb 207,20	83 Bi 209,00	84 Po (210)	85 At (210)	86 Rn (222)						
87 Fr (223)	88 Ra (226)	89 Ac** (227)	104 Ku (258)	105 Ha (260)																			

Main non-metalloids pollutants

Main metalloids pollutants

*Lanthanides

58 Ce 140,1	59 Pr 140,9	60 Nd 144,20	61 Pm (145)	62 Sm 150,4	63 Eu 152,0	64 Gd 157,3	65 Tb 158,9	66 Dy 162,5	67 Ho 164,9	68 Er 167,3	69 Tm 168,9	70 Yb 173,0	71 Lu 175,0
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**Actinides

90 Th 232,00	91 Pa 231,00	92 U 238,00	93 Np 237,0	94 Pu 239,1	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (258)
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Periodic Table of the Elements

> Other inorganics pollutants (synthetic)

> nitrates and nitrites

- Origin: fertilizer industry; agricultural spreading
- Highly soluble in water

> fluorides

- Origin: chemical industry; aluminium metallurgical plant
- Soluble & stable

> cyanides

- Origin:
 - Undesirable industrial by-products (coking technology, gas plant, organic chemistry) ; washing water from blast furnaces, petrochemical (plastics, pesticides, dyes).
 - Starting materials and/or reagents (surface treatment, ores of gold and silver treatment).
- Soluble, fast degradation by soil acidity

Different types of micropollutants – chemical family

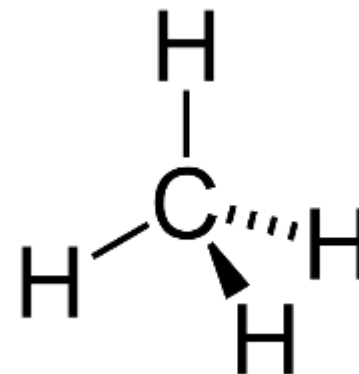
> Organic micropollutants

- Any chemical compound that contains carbon. Due to carbon's ability to catenate (form chains with other carbon atoms), millions of organic compounds are known.
- Methane, CH₄; it is one of the simplest organic compounds.
- More often « Anthropogenic pollutants »

⇒ Industrial compounds

⇒ Phytopharmaceutical products (PPPs) - pesticides

⇒ Urban pollutants ...



Main organic pollutants families:

> Industrial organic pollutants

- Hydrocarbons: gasoline, diesel, fuel, tar... that contain different molecules (VOCs, BTEX, PAHs...)
- Industrial solvents: BTEX, VOCs...,
- PCBs : polychlorobiphenyls
- Phenols, Detergents....

<u>Benzene</u>	B
<u>Toluene</u>	T
<u>Ethylbenzene</u>	E
<u>Xylenes</u>	X

> Agricultural organic pollutants

- Nitrates : manure spreading...
- Phytopharmaceutical products PPPs...(fungicides, herbicides, growth hormone....)
- Veterinary products
- Disinfectants...

> Urban organic pollutants

- Pharmaceuticals products
- Personal care products,
- Hydrocarbons (PAHs) gas of cars, pesticides.....



> **Emerging pollutant = unregulated molecule for which our concern/interest is growing**

- New substance on the market
- Newly discovered in the environment
 - Increase of knowledge
 - Increase of sampling methods
 - Increase of analytical methods
- Adverse effects newly discovered

Emerging compounds can be former molecules!



Compound of Emerging Concern

> **No consistency in term of use or chemistry:**

- Inorganic and organic industrial pollutants: perchlorates, PFAS...
- Non relevant pesticide metabolites: acetochlor ESA & OXA...
- Personal care products, pharmaceuticals: parabens, antibiotics, carbamazepine...

Introduction into the environment:

> 3 main sources of pollution:

- ⇒ Industrial activities, that use water for products and emit effluents
- ⇒ Agricultural activities, when manure, fertilizers and pesticides are spread to the fields – water run off and infiltration into soils toward rivers and groundwater – Leakage of phytopharmaceutical products, tank flushing...
- ⇒ Urban activities, from the sanitation network, use of pesticides, vehicles, domestic heating, domestic consumption...

> Distinction between

Point source pollution

originates from discrete locations whose inputs into aquatic systems can often be defined in a spatially discrete manner

Diffuse pollution

originates from poorly defined, diffuse sources that typically occur over broad geographical scales

Patterns of pollution regarding the type of sources

Sources	Diffuse pollution	Point source pollution
industrial	+	+++ Industrial wastewater
agricultural	+++ Pesticides' spreading, manure, fertilizers...	+ Tank leakage
urban	+ WWTP sludge, storm-water and urban runoff...	+++ Waste water treatment plant effluents

Ubiquitous pollutants

Multi sources, rainfall...

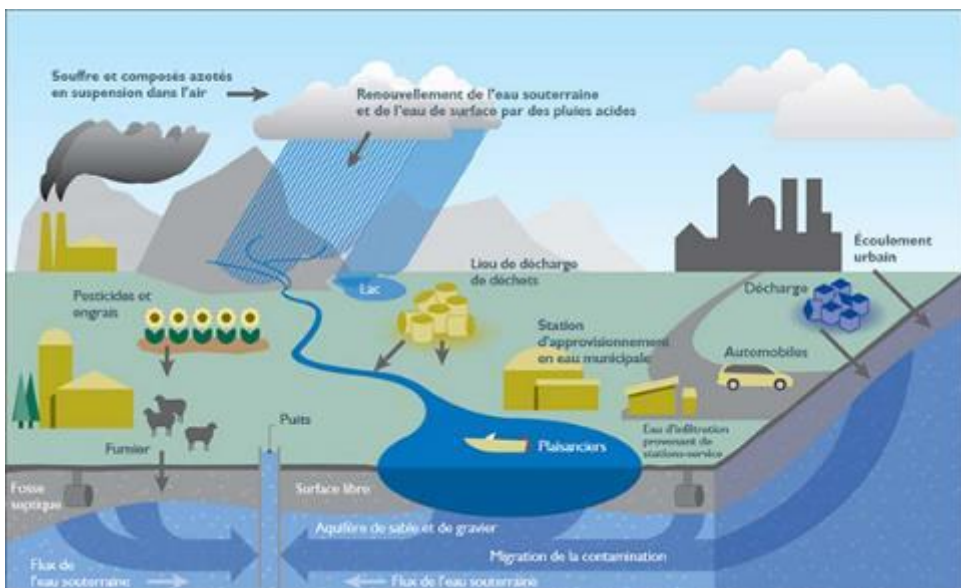
Issues regarding groundwater resources

> An impressive number of chemical products on the market

- In 2017, the European Chemical Agency (ECHA) listed **106,211 individual chemicals** manufactured or imported on the European market since 1971
<https://echa.europa.eu/fr/information-on-chemicals/ec-inventory>

> Large variety of sources, pathways and fate

- In the environment
- In treatment plant systems



Source : Pollution Probe – The Source Eau Protection Primer 2004

> What are micropollutants of higher concern?

> Which micropollutants to survey in priority?

> How to reduce emission to the environment?

> How to remove from water resources?

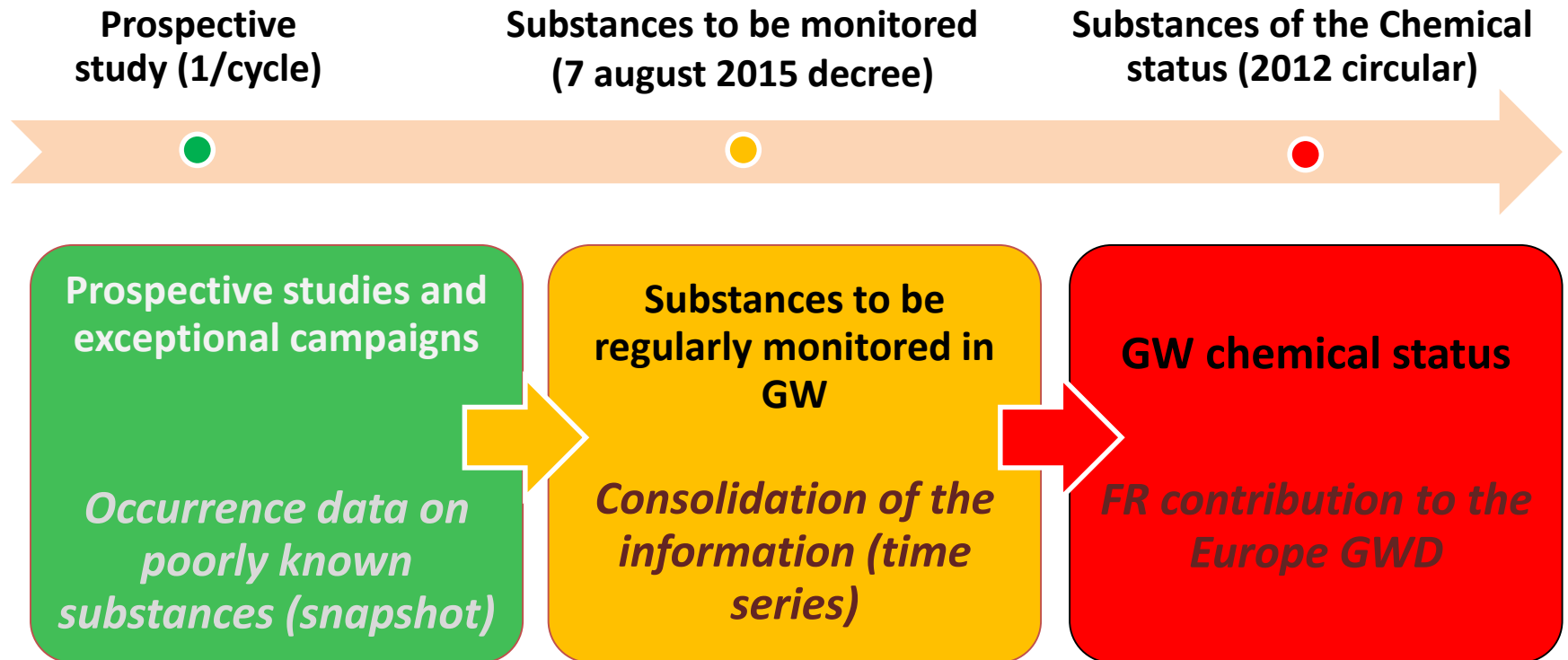


PRIORITISATION OF MICROPOLLUTANTS IN GROUNDWATER

A need: To identify micropollutants to be monitored in aquatic systems and groundwater in particular

A method organized in a 3 steps cycle

> French groundwater regulatory surveillance



« Cycle » following the River Basin Management Plant definition = 6 years

Behind the very high and increasing number of manufactured chemicals emitted in the environment it is impossible to assess and monitor all substances

=> Need to prioritise micropollutants

> Prioritisation = a management solution

- Conclusion of the « Managing Contaminants of Emerging Concern in Surface Waters”

[OECD Paris Feb. 2018](#)

⇒ To target and put plan of measure in practice

⇒ To adapt treatment plans

⇒ To identify substances to be monitored

106,211 chemical substances
identified in the EU in 2017

*ECHA Database contains 13,052
unique substances and contains
information from **50,405***

Dossiers (last updated 25
February 2015)

Why to prioritise micropollutants in water resources?

> To conform the regulation (WFD and GWD)

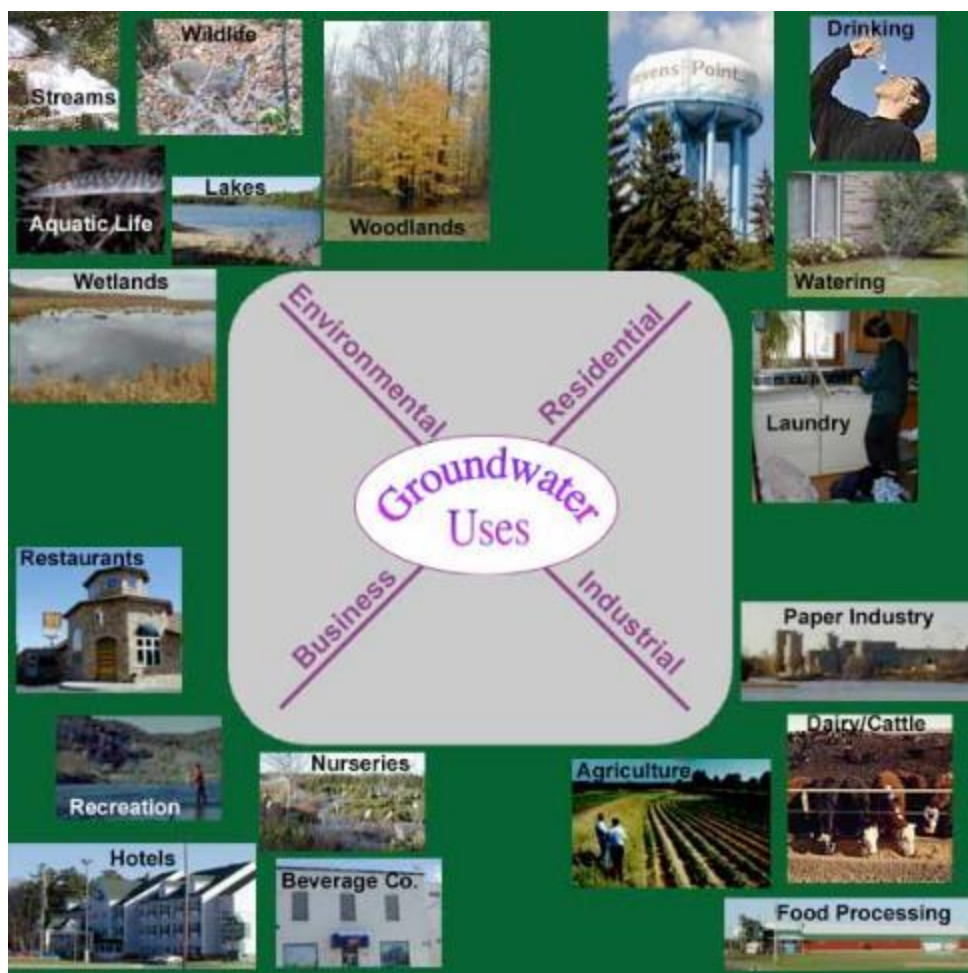
- WFD 2013/39/EU “Review the list of substances designated as Priority Substances and Priority Hazardous Substances”
- Recital (4) of the GWD 2014/80/EU states the need “to obtain and respond to new information on other substances posing a potential risk [...] to groundwater”.

> Choices have to be made

- to focus on certain substances among all existing chemicals
- to come to consensus about key/priority substances regarding environmental and/or health protection objectives

⇒ **Groundwater is a specific middle of the aquatic environment**

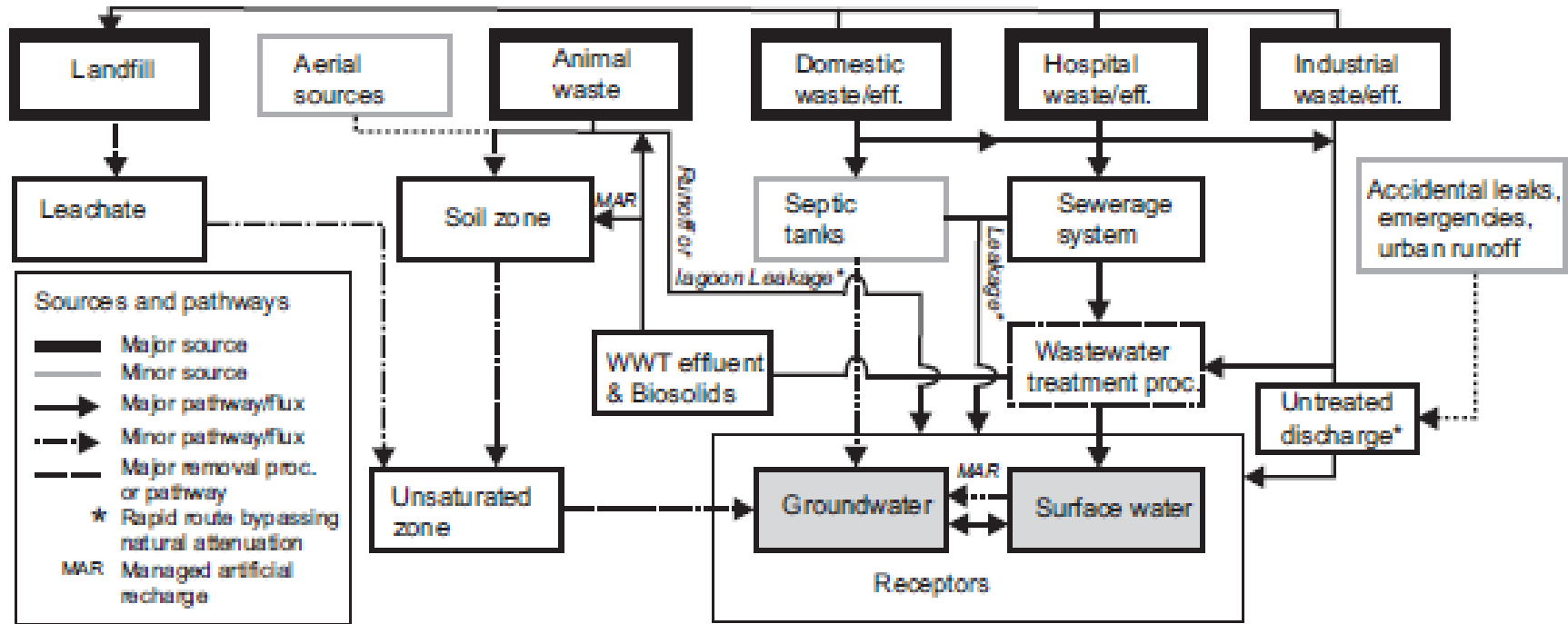
➤ There are many different uses of GW resulting in different objectives of resource protection



This collage only represents a few uses of groundwater

- Water supply
- Irrigation
- Industry
- GW Dependent or Associated Ecosystems
- ...

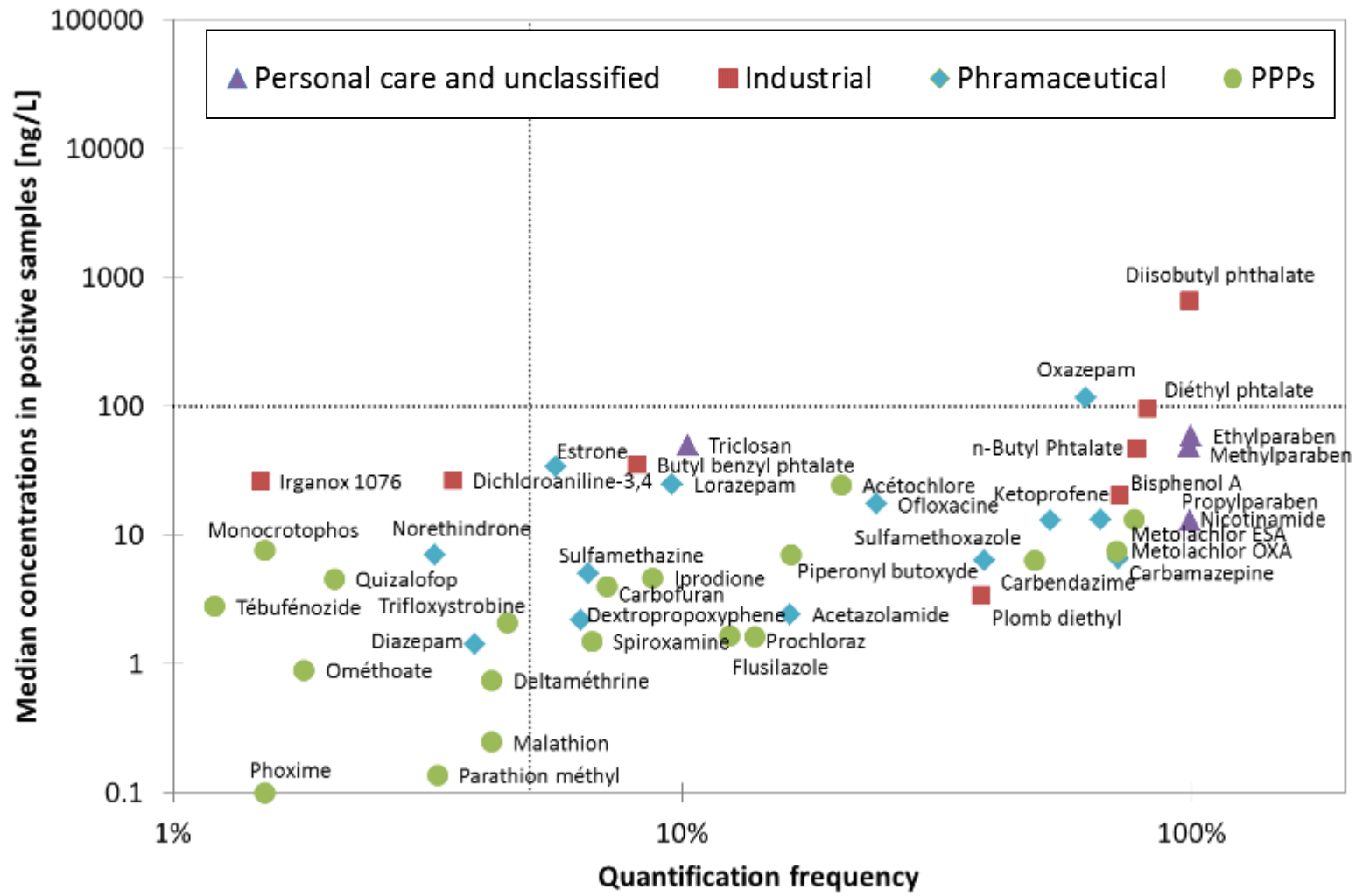
- > For many micropollutants there may be multiple pathways to groundwater and associated receptors



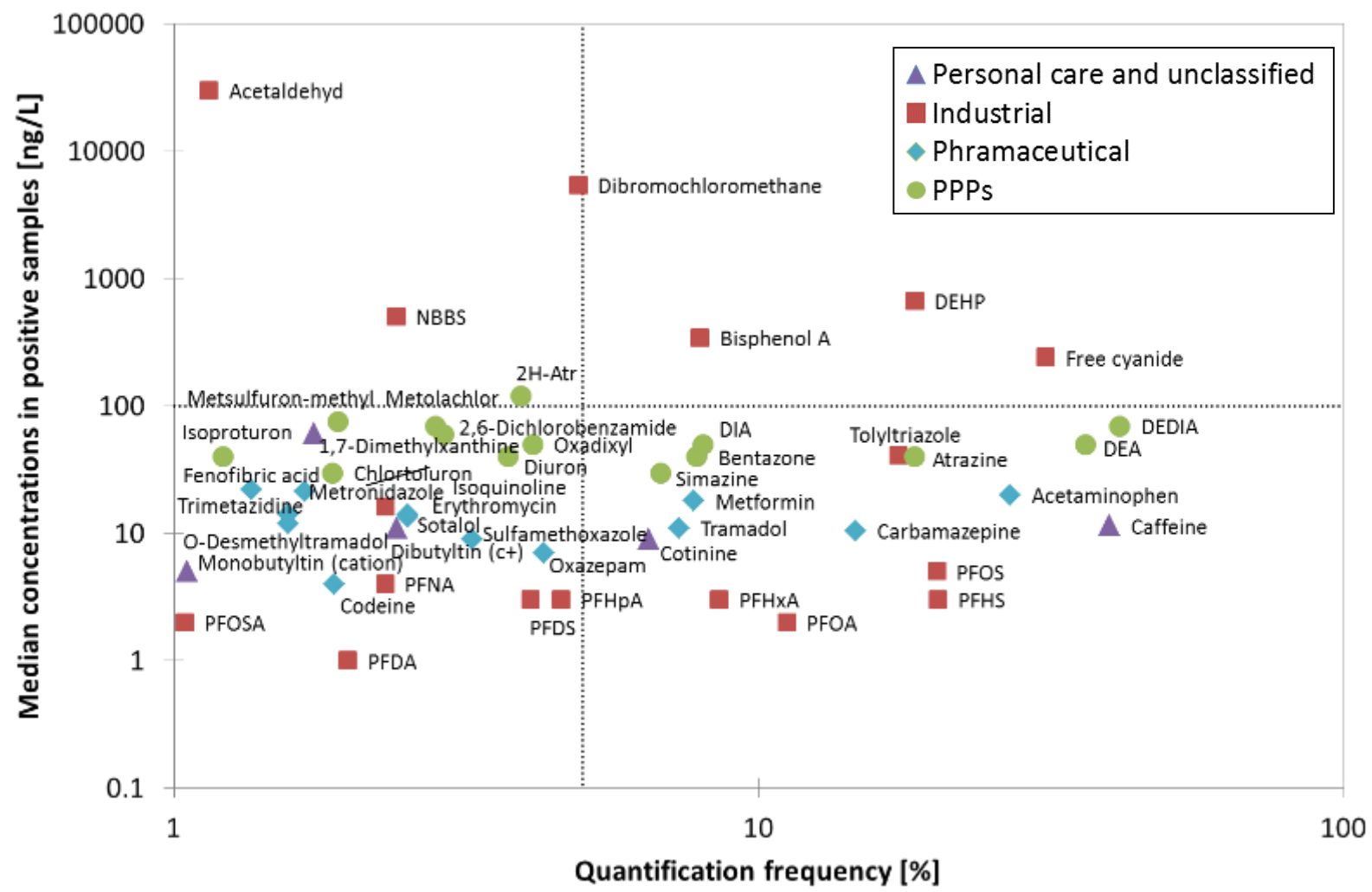
Processes that should affect the nature of groundwater pollutants:
Leaching, retention, attenuation, partial degradation, transformation...

Schematic diagram, using the source-pathway-receptor approach, highlighting potential sources and pathways for groundwater pollution by EOCs (Lapworth et al., 2012)

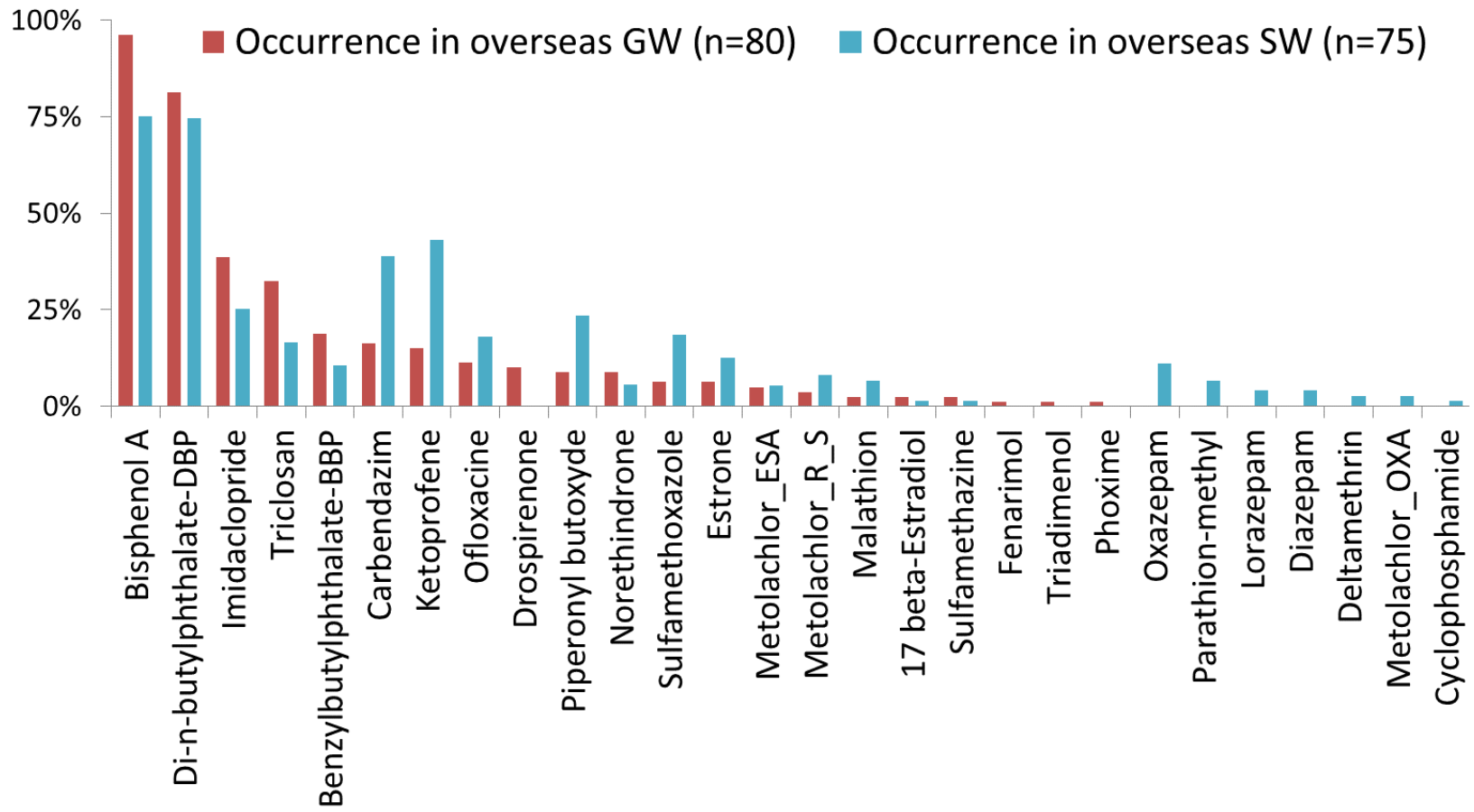
- > Different pathways for GW and SW pollution result in different substances expected in GW and SW
- > Ex. 2012 Screening of ECs in Fr. surface water (n=29,280)



> 2011 Screening of ECs in **Fr. groundwater** (n=393,191)

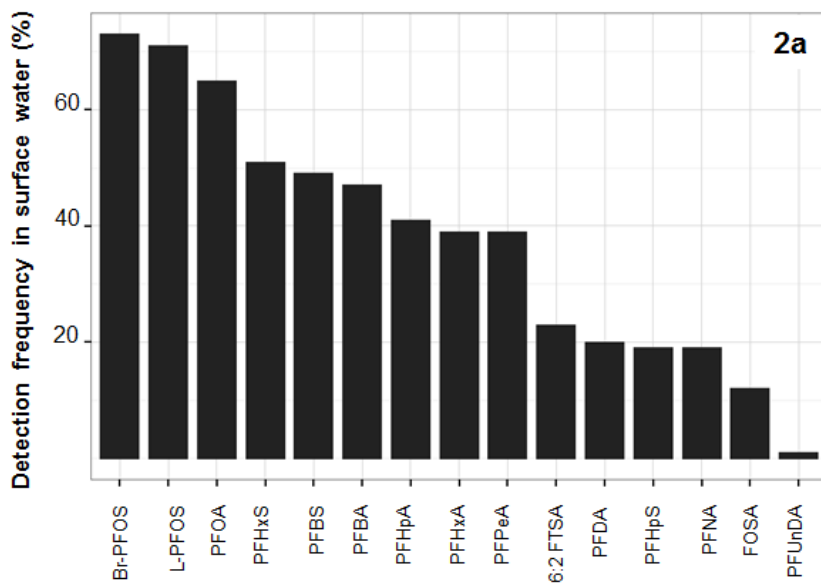


Ex. French overseas 2012 SW and GW ECs campaigns
 same labo., same LOQ, same sampling period - 51 common ECs

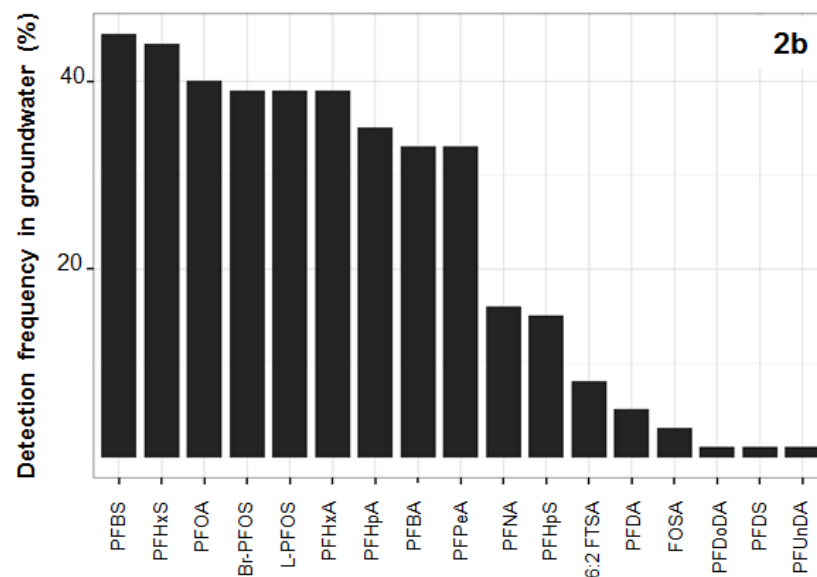


- Within a same family (same uses), there are not the same compound occurrences in surface and groundwater
- Ex. of poly and perfluoroalkyl substances (PFAS) in Overseas France (Munoz G. *et al.* 2017; STOTEN)

Overseas surface waters (n=75)



Overseas groundwater (n=80)



- Long-chain PFOS and PFOA prevailed in surface water Vs. short-chain PFBS, PFHxS and PFHxA in groundwater

Principle of the prioritization of micropollutants in groundwater

- > **Identification of micropollutants of high importance in groundwater**

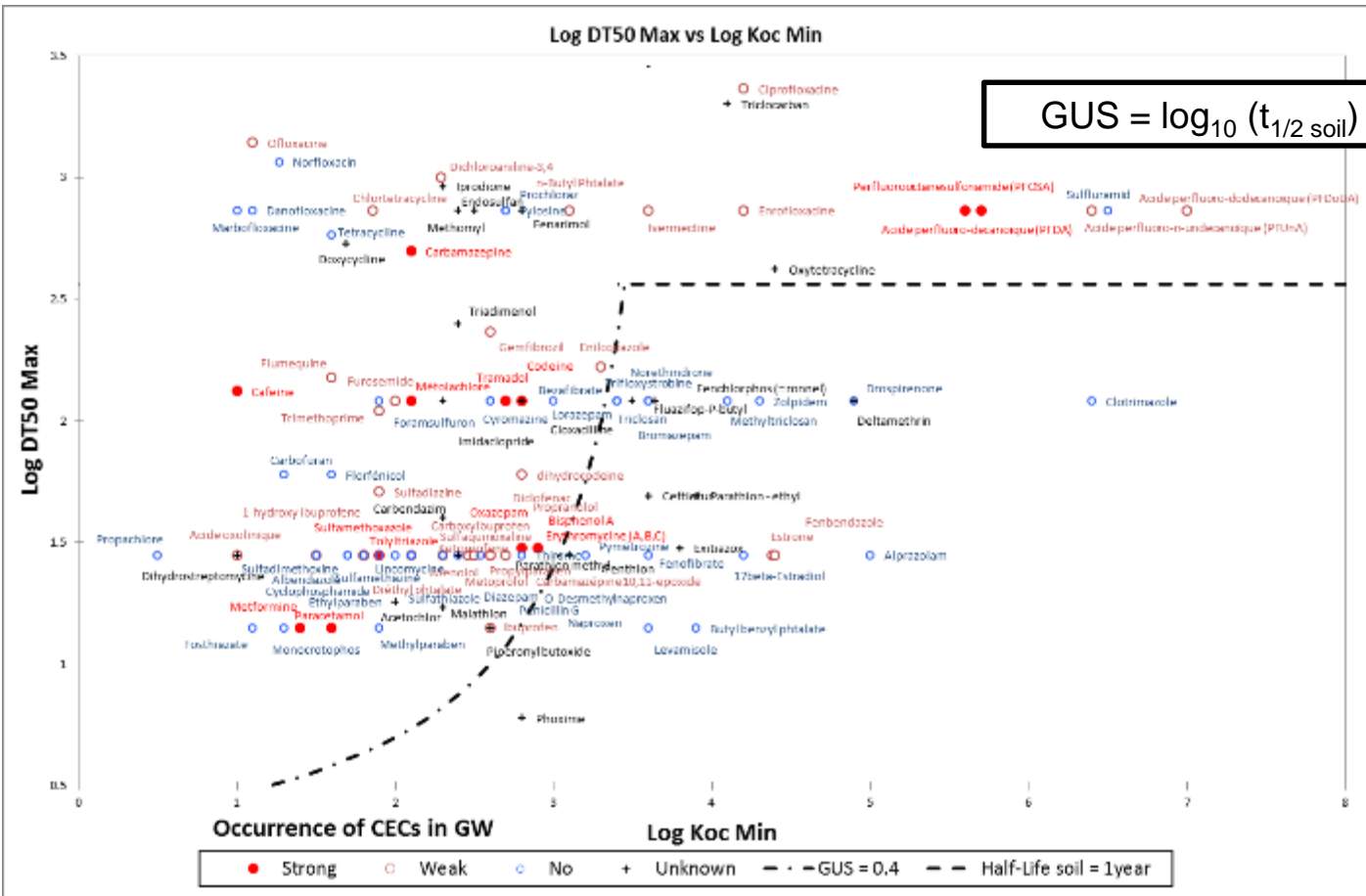
- > **Criteria:**
 - Leaching potential to GW
 - Health and/or environmental hazard
 - Others? Ease of analysis, treatability, possibility to regulate (withdraw from the market, substitution molecules)

- > **Limit of the method**
 - Data availability
 - properties (mobility, degradability and toxicity and eco-toxicity)
 - usage at the EU scale (confidentiality of industrial data)
 - Estimation of the leaching potential of micropollutants

- ⇒ Development and test of novel indicators

Exemple: Leaching Potential to GW graphical assessment

- > Potential leachers = all substances with $DT_{50\text{soil}} > 1\text{year}$ and, if not substances for which $GUS > 1.4$



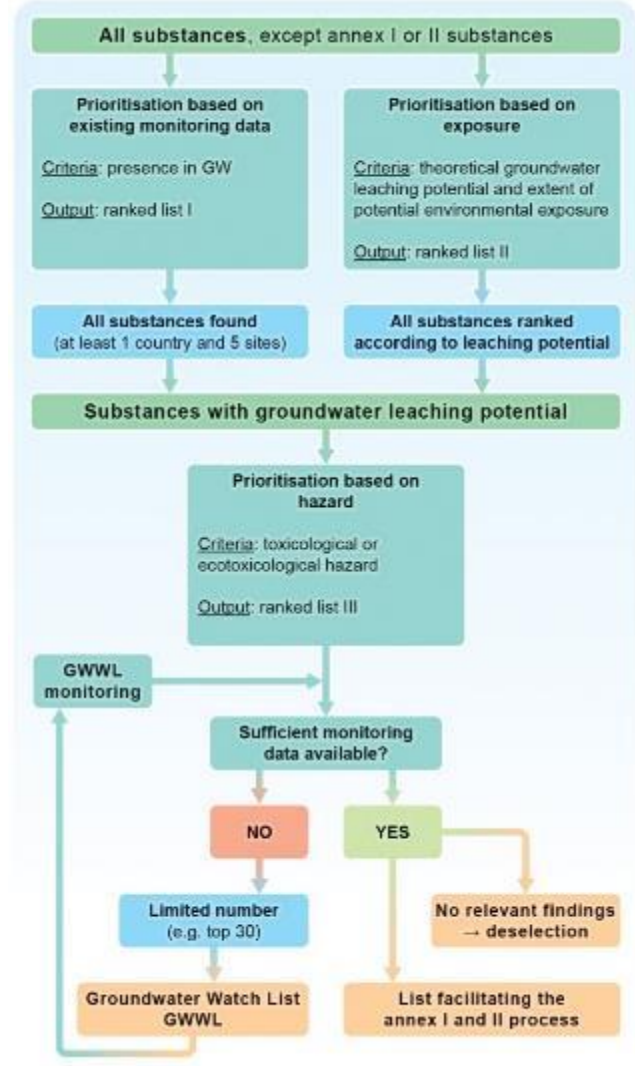
$\log(t_{1/2\text{ soil}}) = f(\log(Koc))$ diagram for CECs for which $t_{1/2\text{ soil}}$ and Koc properties are available. Occurrence in GW comes from Lopez, B., et al. (2015).



Ex1. GW Watch List concept

European initiatives

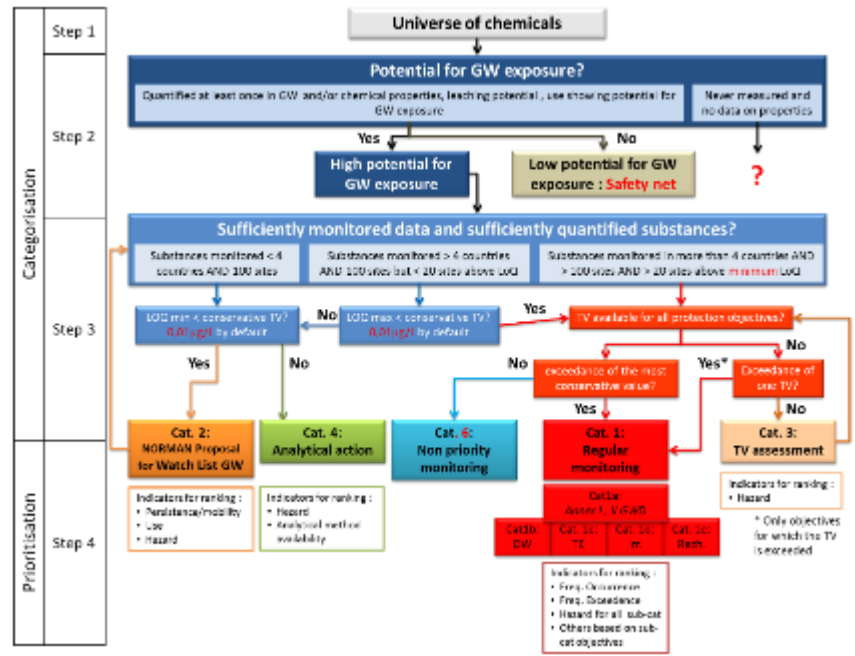
- Methods that combine and aggregate
 - occurrence data
 - chemical properties
- ⇒ prioritisation GW leaching potential and hazard



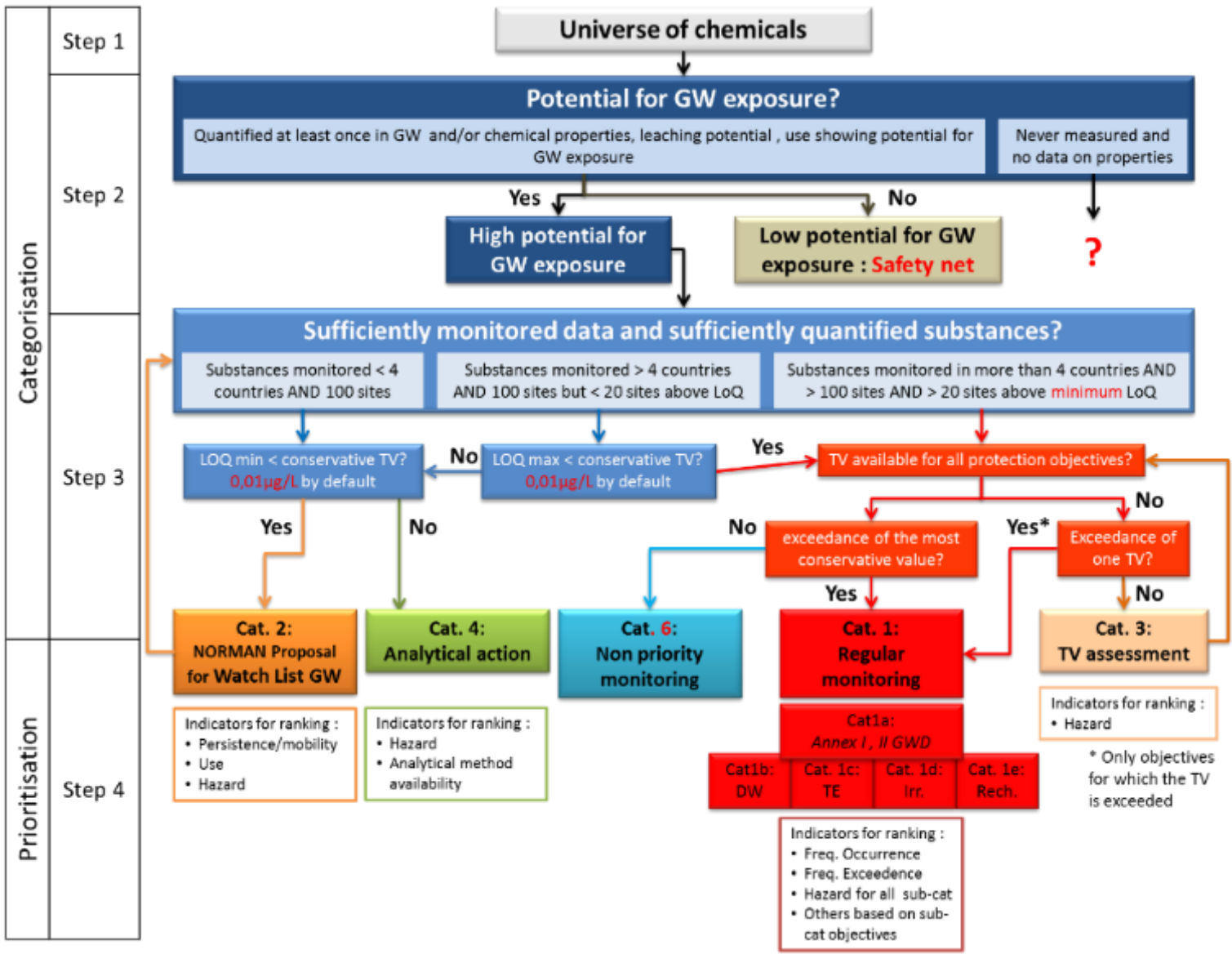
Lapworth et al., ERL 2018, accepted



Ex2. NORMAN decision tree for GW



NORMAN decision tree for GW

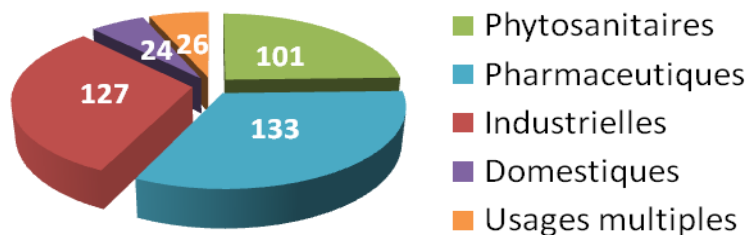




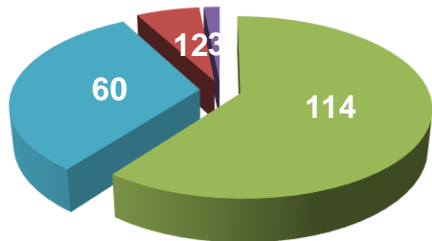
PROSPECTIVE AND REGULATORY SURVEILLANCE OF FRENCH GROUNDWATER

2011-2012 « Exceptional campaigns » in French groundwater

- 411 substances sought in French metropolis

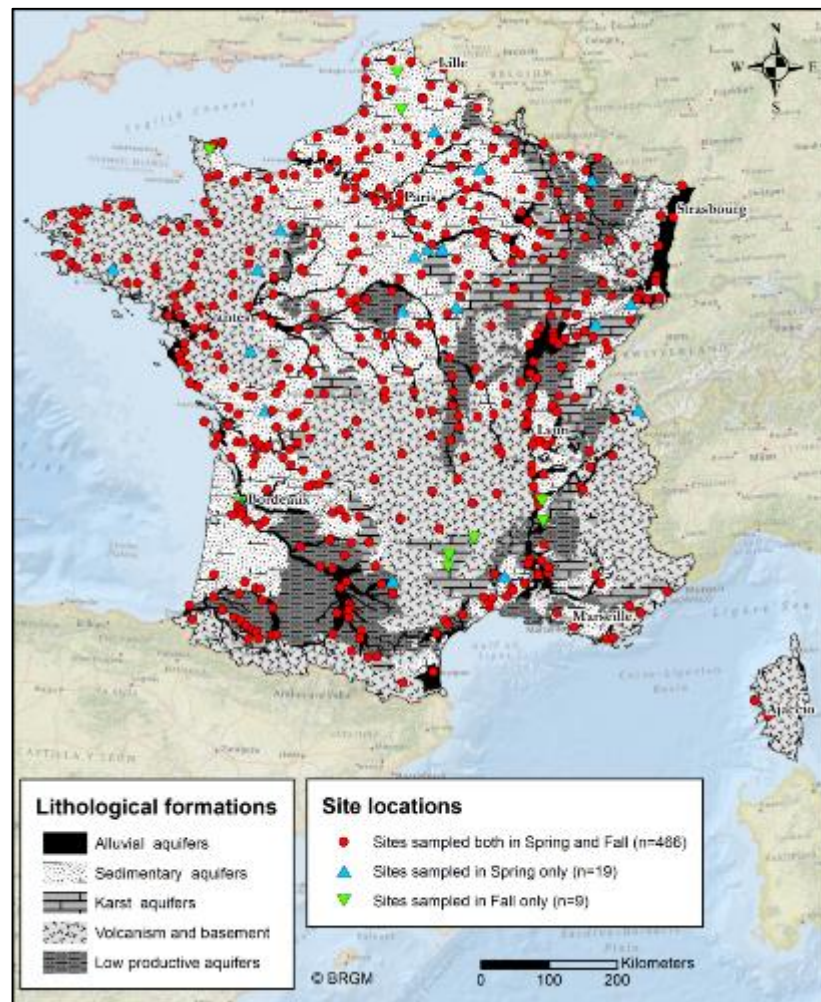


- 189 substances sought in overseas



- 494 sampling sites in French metropolis
- 40 sampling sites in overseas
 - 2 sampling campaigns

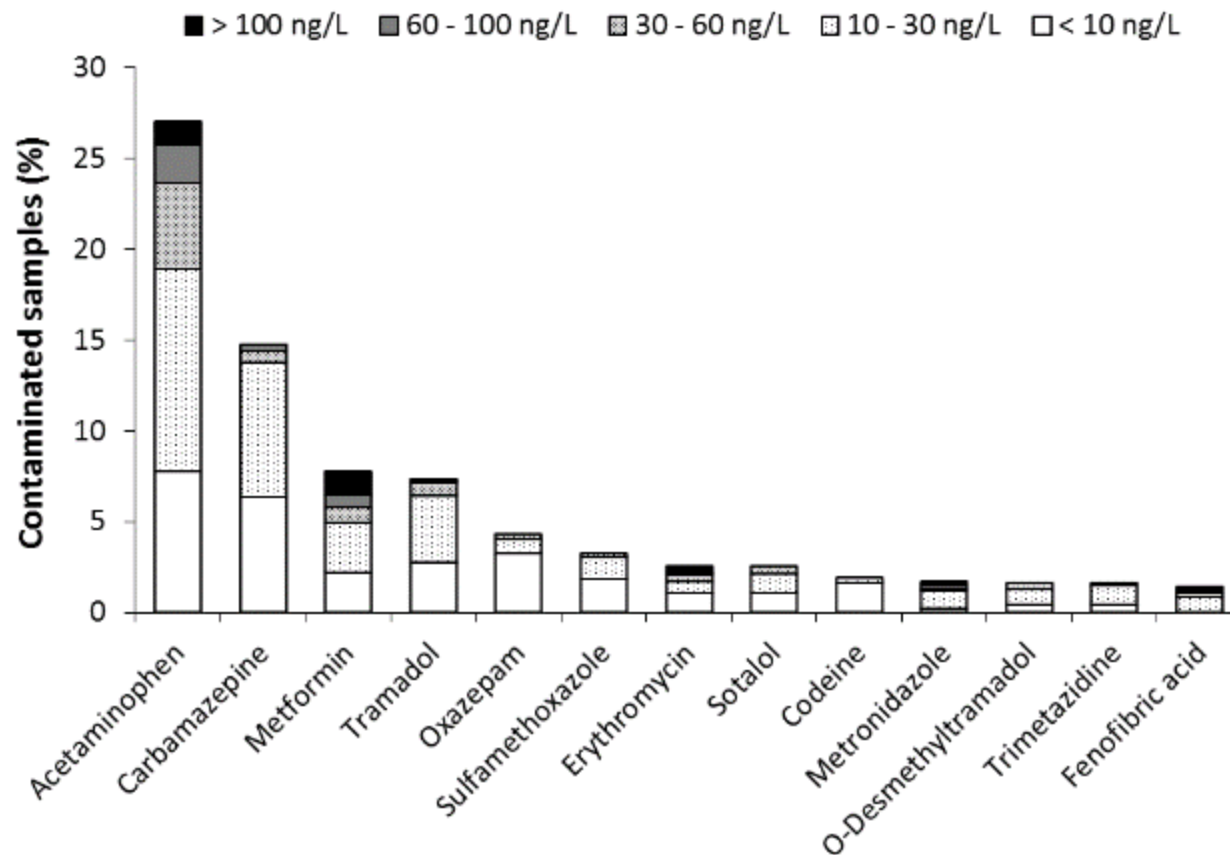
393 191 results in French metropolis
15 280 results in Overseas



Public results available on the groundwater national portal ADES: <http://www.ades.eaufrance.fr/>

Results by use of micropollutants

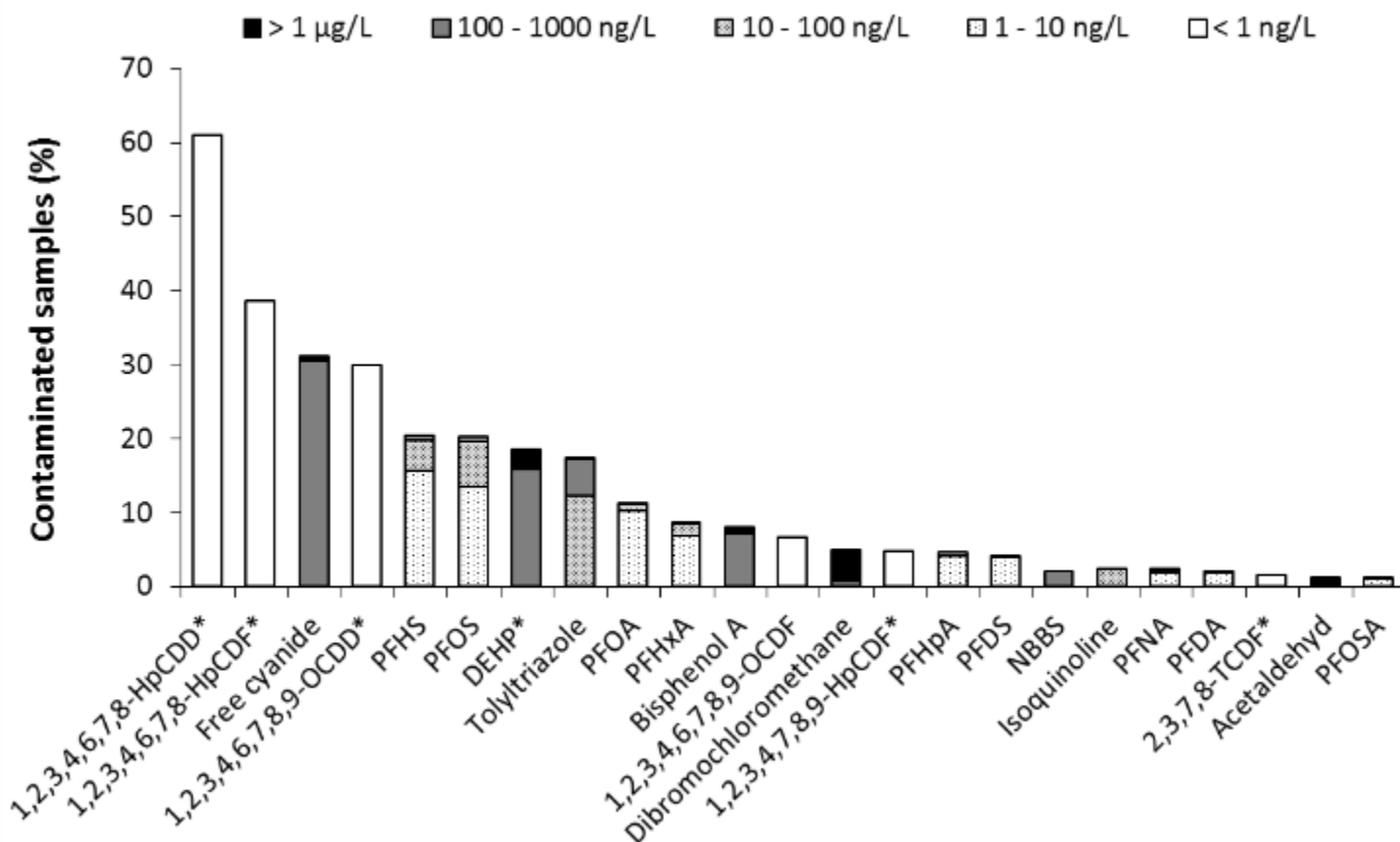
- Pharmaceutical products



Frequency of quantification and levels of concentration for pharmaceutical products quantified in more than 1% of overall samples (n = 954)

Results by use of micropollutants

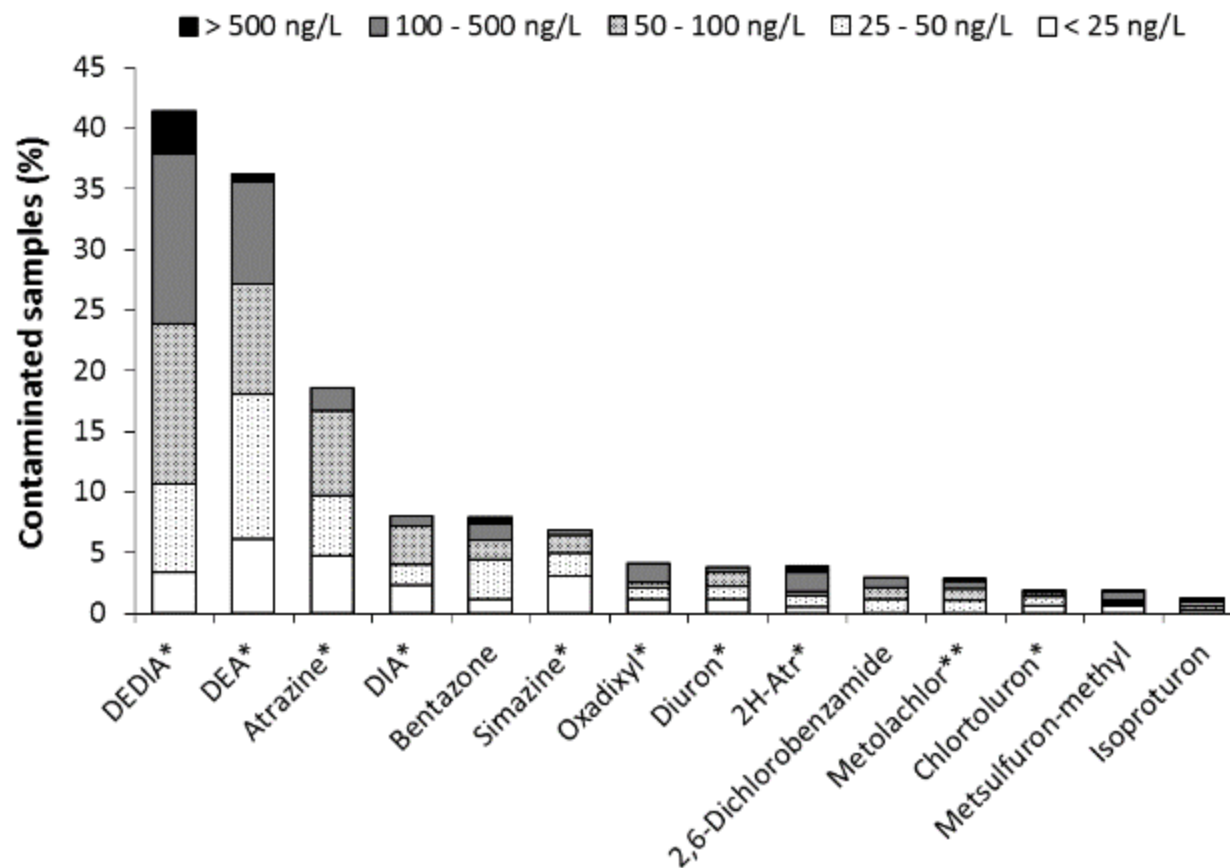
- Industrial compounds



Frequency of quantification and levels of concentration for industrial compounds quantified in more than 1% of overall samples (n = 954); * Mentioned as Priority Hazardous Substances in the WFD (Appendix 2 2013/39/EU)

Results by use of micropollutants

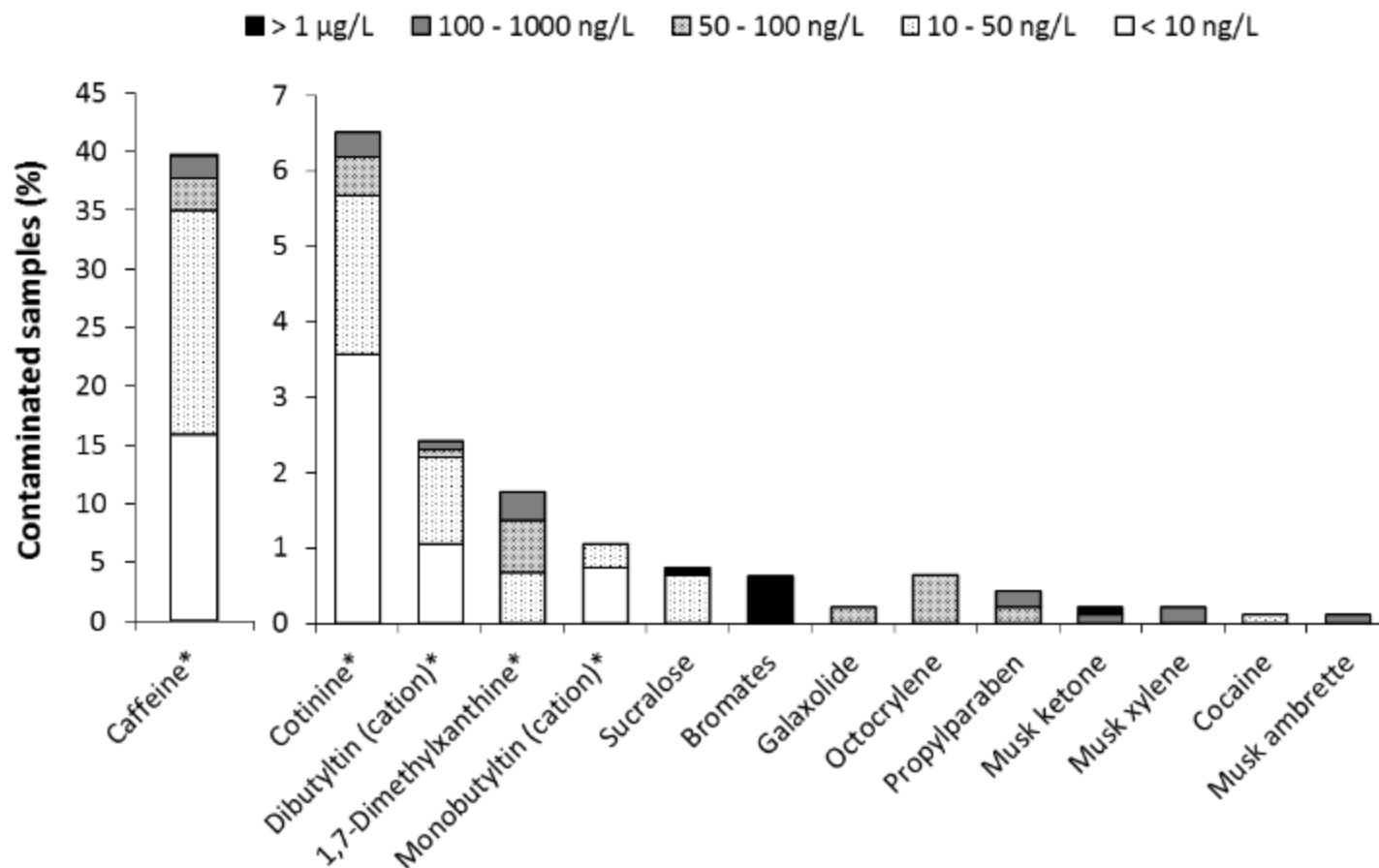
- Phytopharmaceuticals products



Frequency of quantification and levels of pesticides quantified in more than 1% of overall samples; * Withdrawn or transformation product of a withdrawn parent molecule; ** S-metolachlor isomer approved only

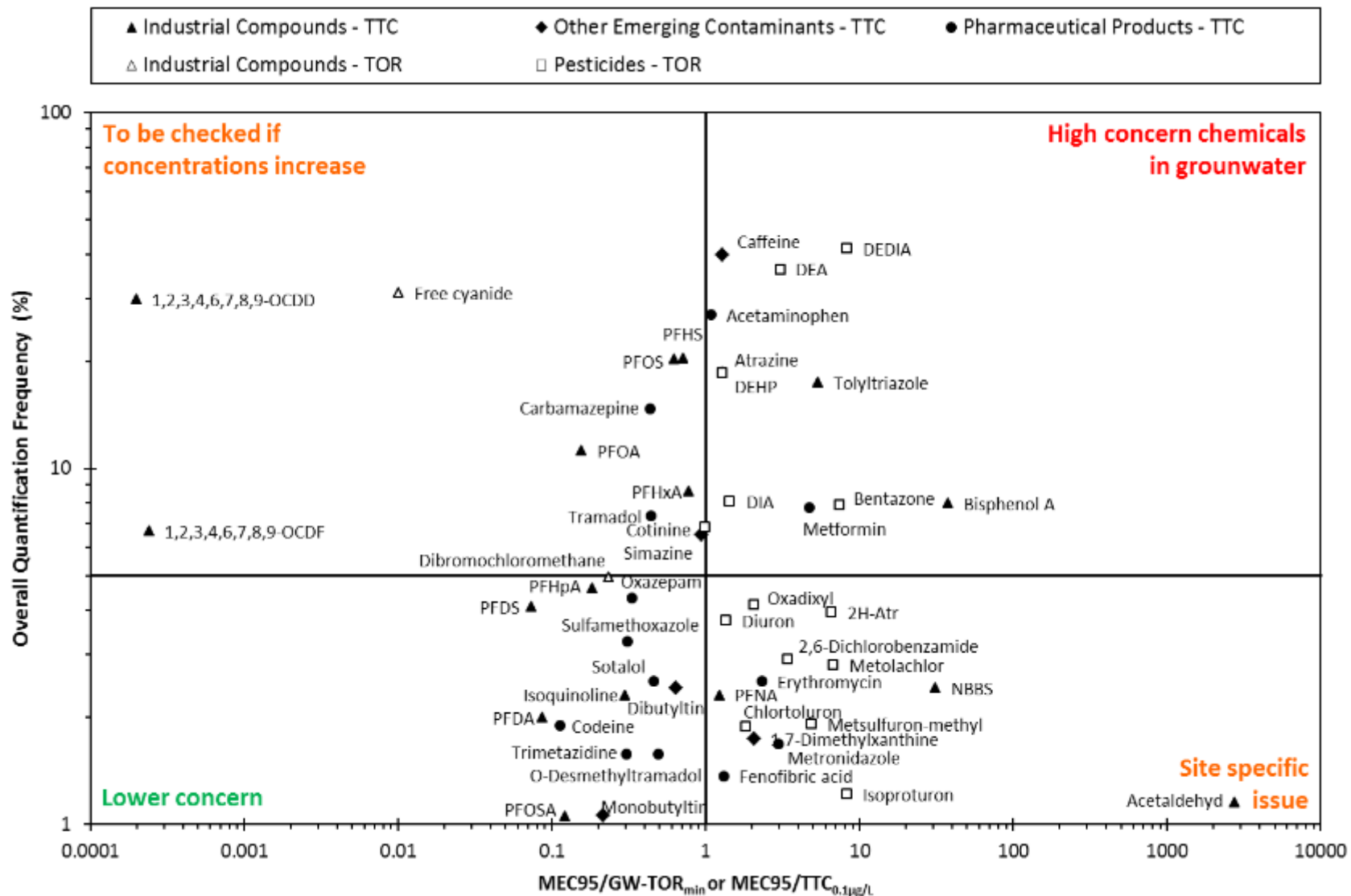
Results by use of micropollutants

- Other compounds of emerging concern

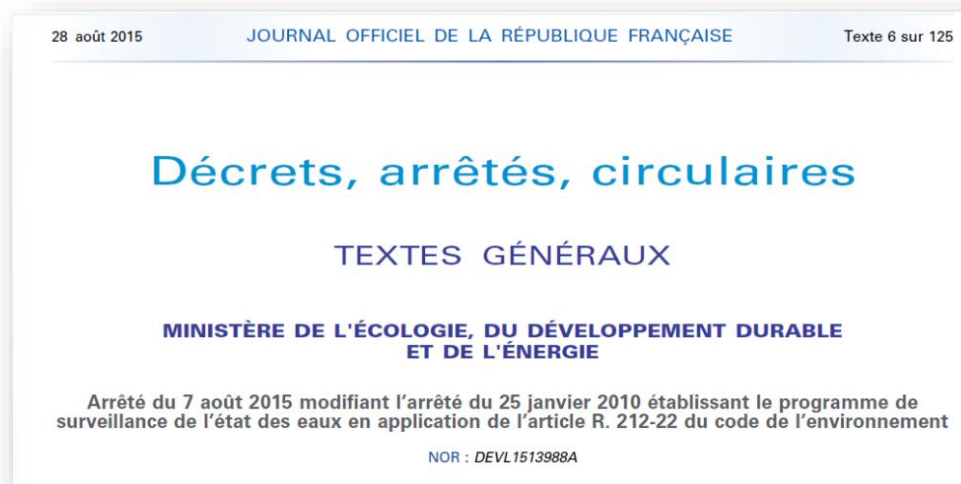


Frequency of quantification and levels of concentration for other emerging contaminants quantified in the overall samples (n = 954); * Quantified in more than 1% of samples

Matrix of quantification frequency and risk of exceedance of toxicological thresholds



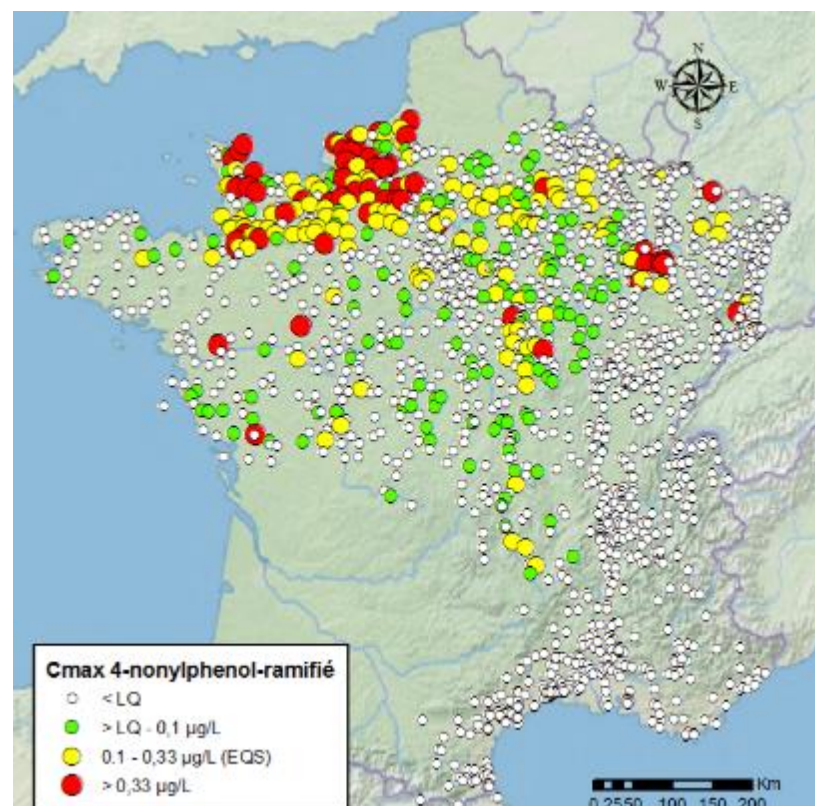
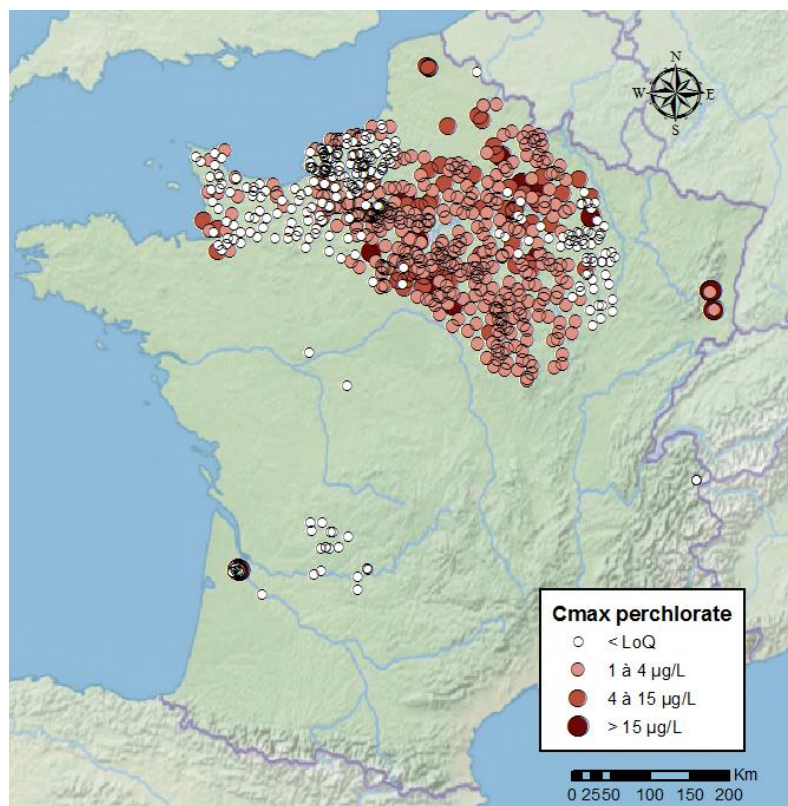
After expert and political judgment and based on these results
=> surveillance Decree of the 7 august 2015



- > Final list: 205 organic compounds, 13 metalloids elements (ETM) and 4 others mineral elements
- > => 223 micropollutants to be regulatory monitored in French groundwater
- > 3 levels of analyses for the regulatory surveillance of groundwater
 - Regular analysis (each years) => 23 micropollutants.
 - Photographic analysis (once per RBMP cycle) => 146 micropollutants.
 - Complementary analysis (twice per RBMP cycle on ¼ of sampling sites) => 54 µpol.

Today: first result of the « new » surveillance (7 of august 2015 Decree)

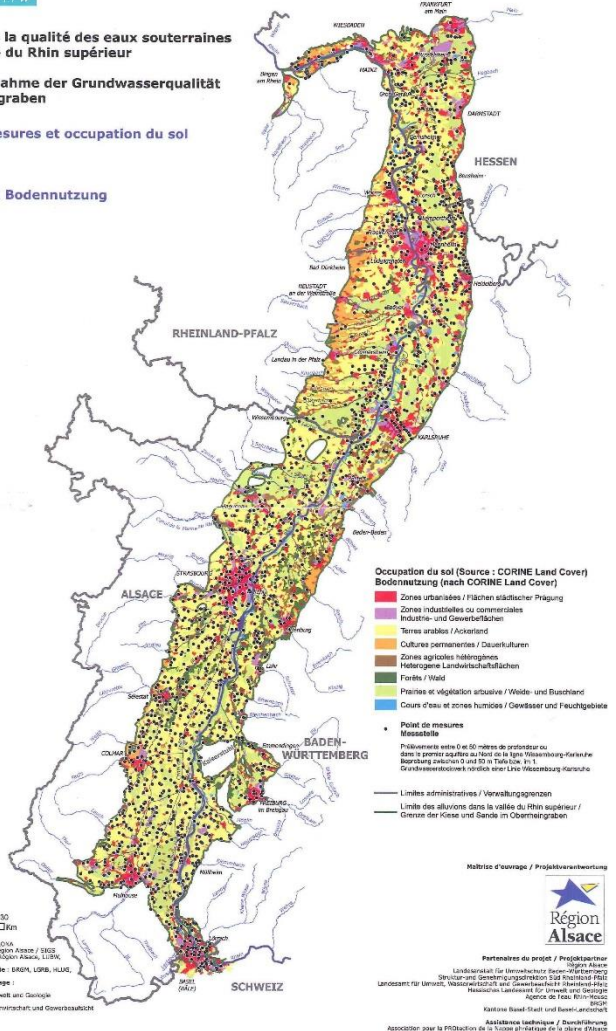
- > Implementation depending on the Water agencies market agendas for chemical analyses
- > Ex. perchlorate & 4-nonylphenol ram. max concentrations
- > Perchlorates : 8 % of sampling with concentrations > 4 µg/l (toxicological threshold for infant and pregnant)



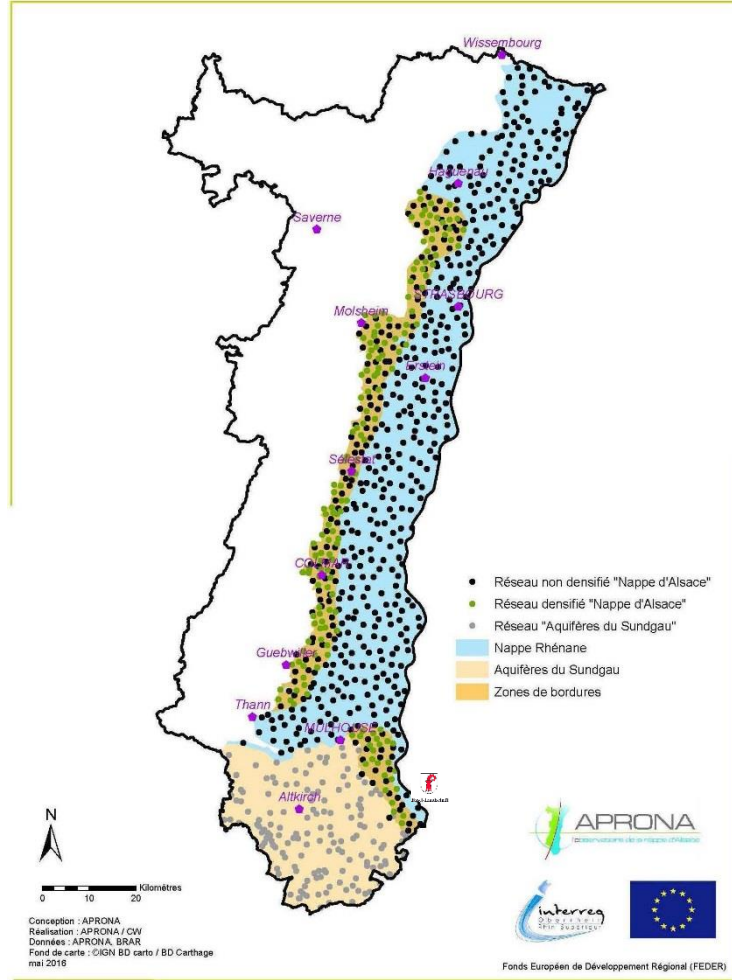
2015-2016: Transboundary study of unregulated and emerging contaminants in Upper Rhine aquifer

CARTE 1 // KARTE 1

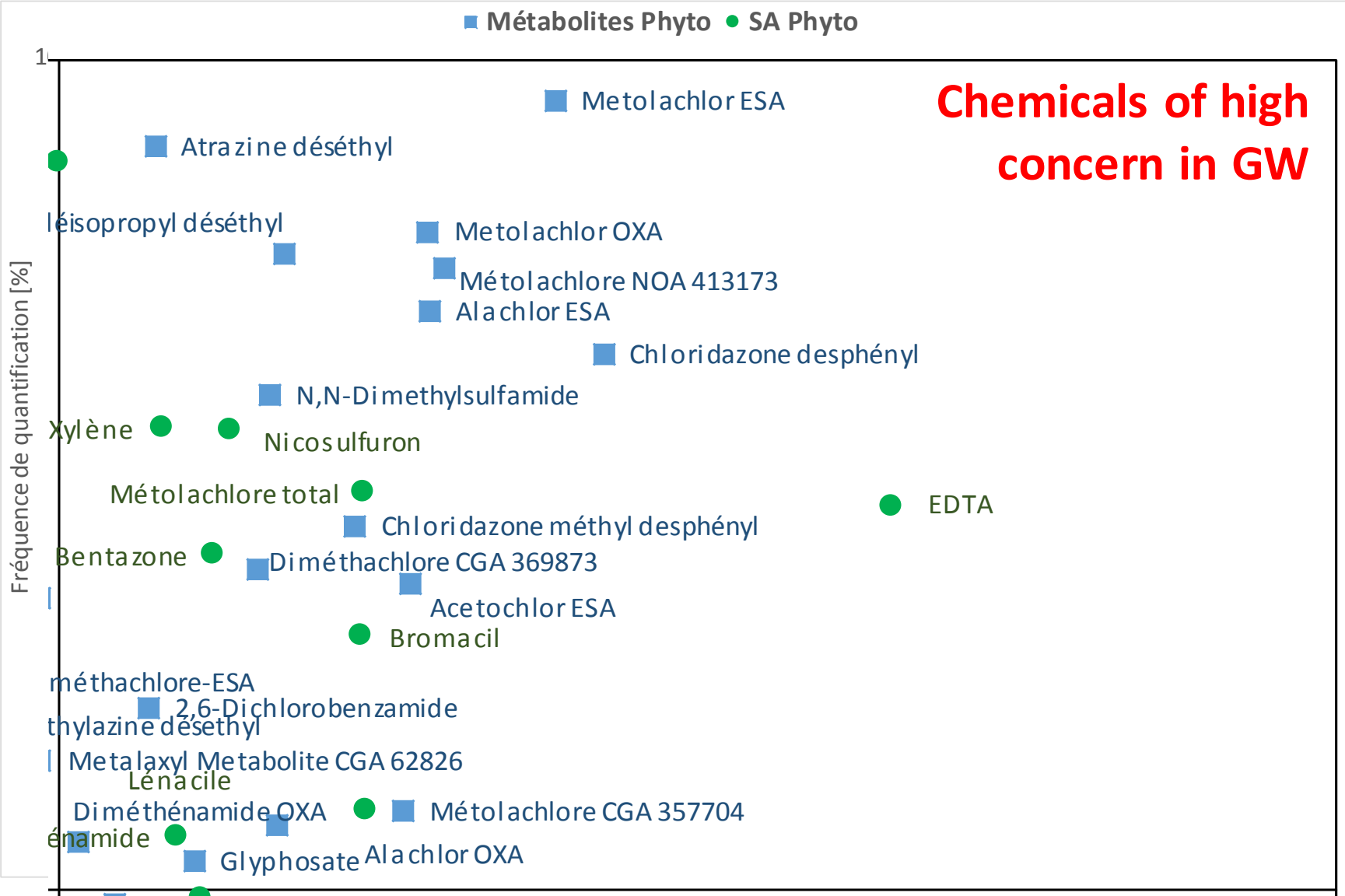
Inventaire de la qualité des eaux souterraines dans la vallée du Rhin supérieur
Bestandsaufnahme der Grundwasserqualität im Oberrheingraben
 Réseau de mesures et occupation du sol
 2009
 Messnetz und Bodennutzung



ERMES-Rhin 2016 - Réseau de mesures (Nappe d'Alsace et Aquifères du Sundgau)



Results on pesticides and their metabolites in the Alsace aquifer



Conclusion and perspectives

> Current initiative

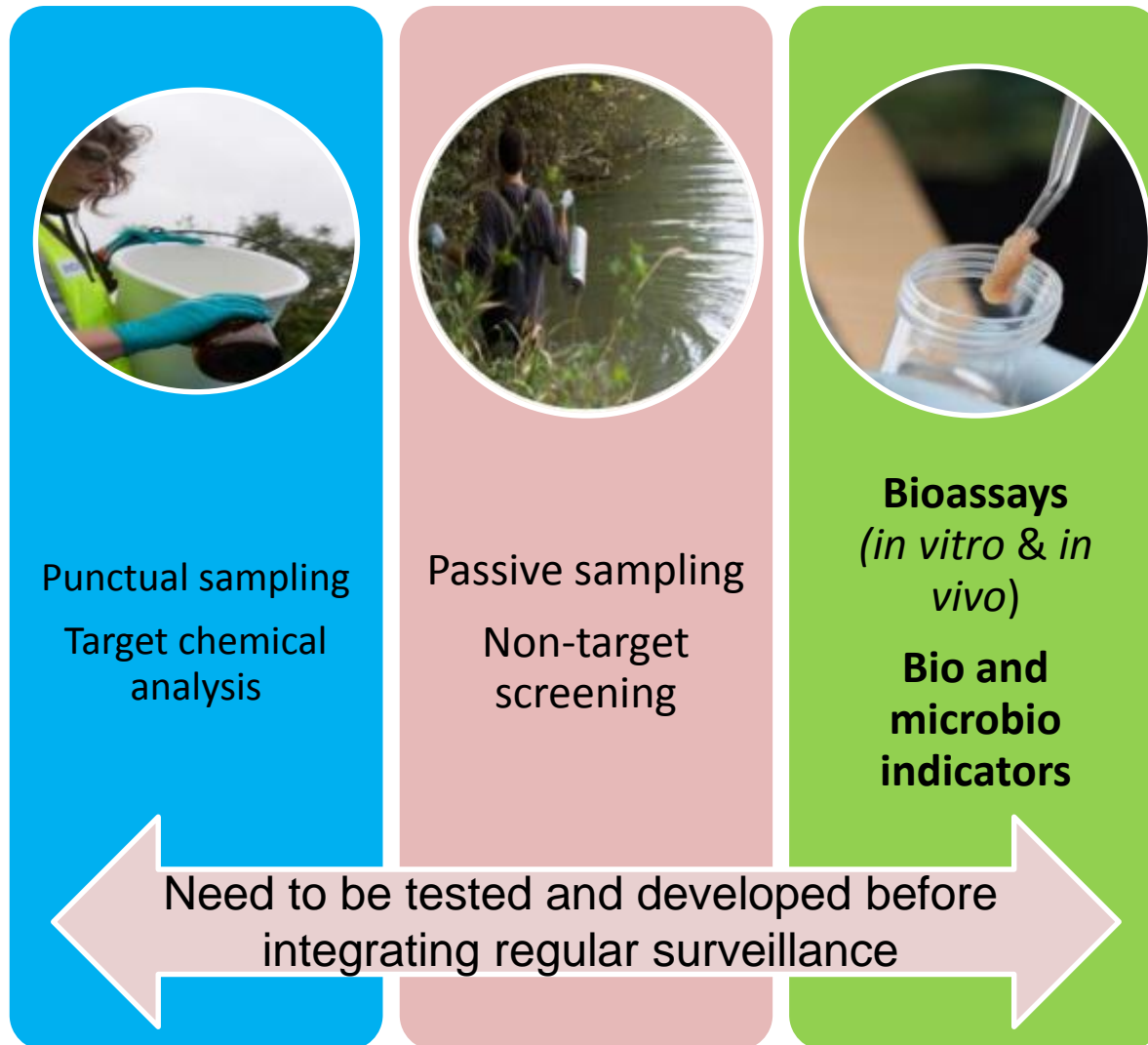
- At the European scale: « Watch List » groundwater
 - CIS GW (Com.)
 - NORMAN
 - GeoERA project – HOVER – WP8 emerging compounds in GW
- At national scale: definition of pesticides relevant metabolites in water supply (ANSES 2019)
- Prospective surveillance
 - 2018-2019: surface water network for prospective surveillance (AFB)
 - 2019: groundwater prospective surveillance (AFB)

> Perspectives

- Reinforce links between health and environment – hazard assessment, threshold values
- Define a robust and relevant scheme for selection and prioritization of micropollutants to be monitored in groundwater to fulfill different objectives
- How to integrate in the regulation new sampling, monitoring and chemical analysis tools?

⇒ **Toward a WFD revision? (2019-...)**

Future surveillance: From classical monitoring and chemical analysis to innovative tools





**THANK YOU FOR YOUR ATTENTION AND
YOUR CONCERN IN MICROPOLLUTANTS**