# Environmental risks associated with the use of registered companion animal parasiticide products: the example of fipronil

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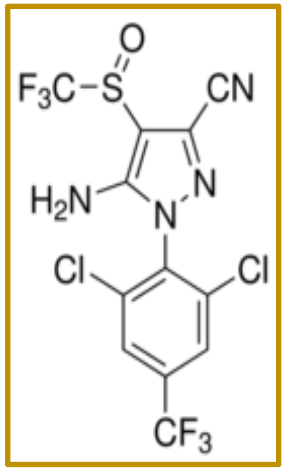
# Presentation outline

- Fipronil usage
- Fipronil measurement in continental waters
- How does it make its way to aquatic ecosystems?
- Fipronil toxicity
- Conclusion
- References
- Questions?



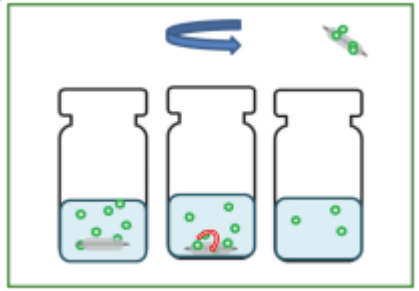
# Fipronil as an insecticide


- Insecticide of the phenylpyrazole family but often associated with neonicotinoids
- Mode of action: binds to the GABA receptors (≠ acetylcholine receptors) ⇨ ↑ central nervous system activity
- Pesticide to treat seeds and crops + hens against red lice; now banned in most European countries
- Used to control ants, beetles, cockroaches, termites (biocide) + **fleas, ticks, lice** (veterinary product)
- Frontline® = one of the most popular veterinary ectoparasiticide

# Fipronil as a water contaminant

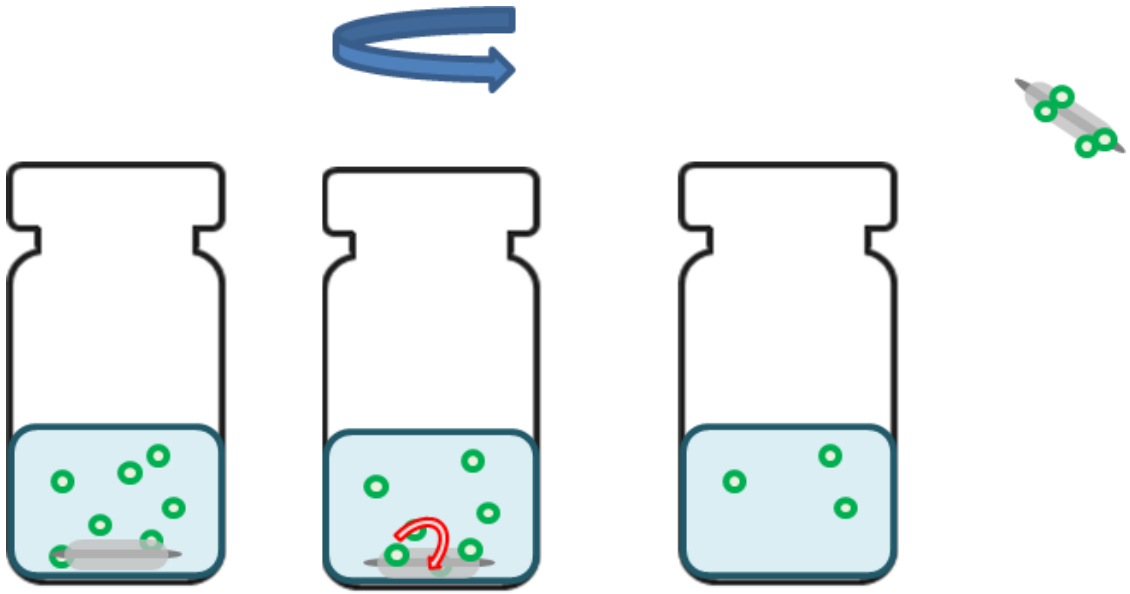
- Historically not detected in the environment ⇐ LOQ = 2-4 ng/L

  ⇨ more sensitive method developed using a SBSE (Stir-Bar Sorptive Extraction) approach + GC-MS/MS : LOQ = 0,1-0,5 ng/L (Cruz 2015)



- Widespread contamination of surface waters in France (Cruz 2015)
  - ➢ Fipronil quantified in 65 % of samples, and fipronil sulfide and sulfone in 57 and 56 % of samples
  - ➢ Fipronil concentrations > Predicted No Effect Concentration (PNEC = 0.77 ng/L) in 37 % of samples.

# Stir-Bar Sorptive Extraction



(Budzinski 2021)

- Same principle as SPME: technique based on the partitioning in a magnetic stir-bar placed in the sample under agitation
- PDMS coating (larger amount than for SPME)

# Stir-Bar Sorptive Extraction


Stirring

Controlled room T°
(20 °C)

5 times of extraction tested
(1, 6, 12, **16** and 24 h)

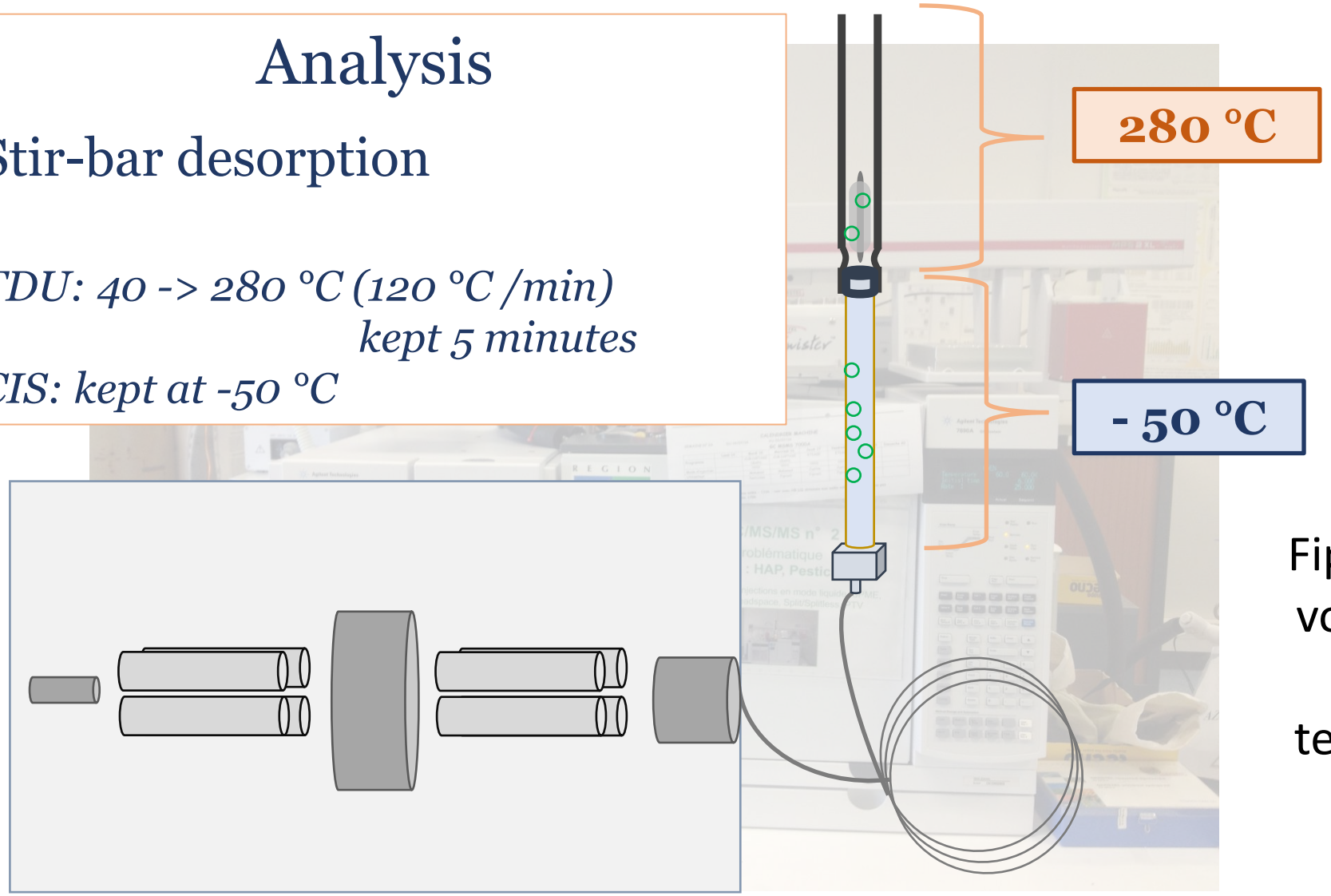
2 volumes of extraction tested
(50 and **100 mL**)

# Stir-Bar Desorption

## Analysis

### Stir-bar desorption

*TDU: 40 -> 280 °C (120 °C /min)*
*kept 5 minutes*
*CIS: kept at -50 °C*



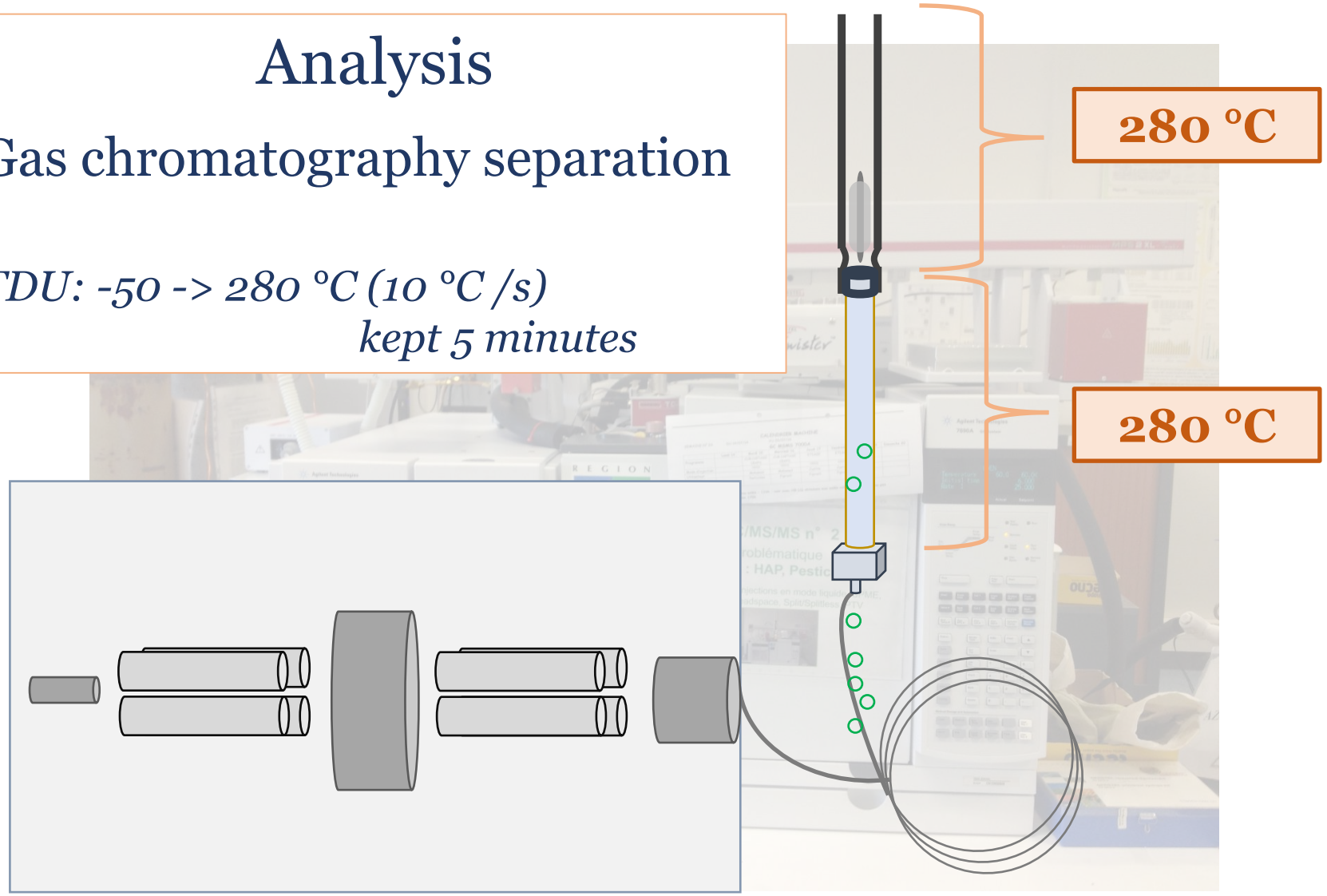

Fipronil sufficiently volatile and stable for this temperature to be used

# Stir-Bar Desorption

## Analysis

Gas chromatography separation

*TDU: -50 -> 280 °C (10 °C /s)*
*kept 5 minutes*

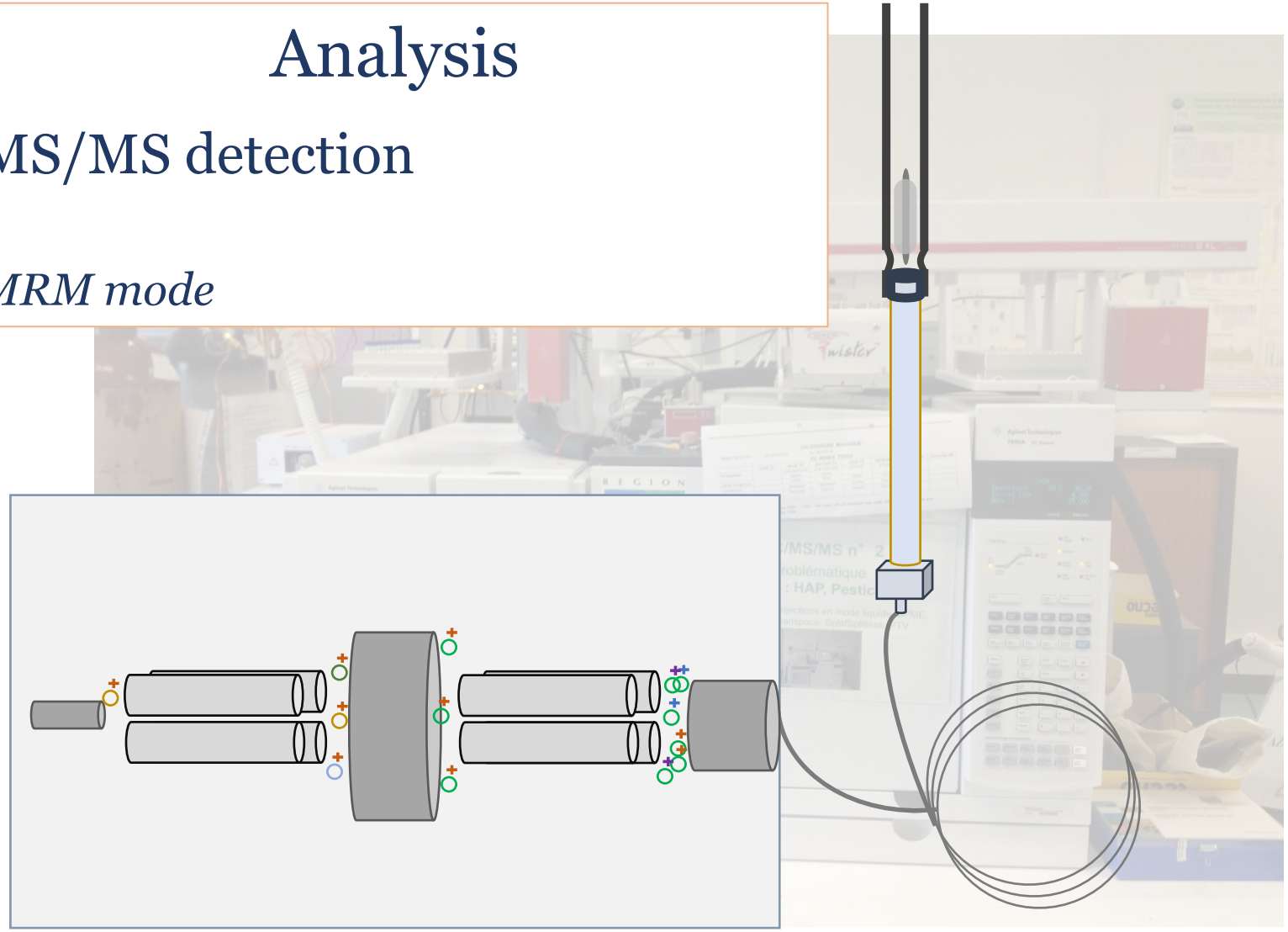


# Fipronil detection

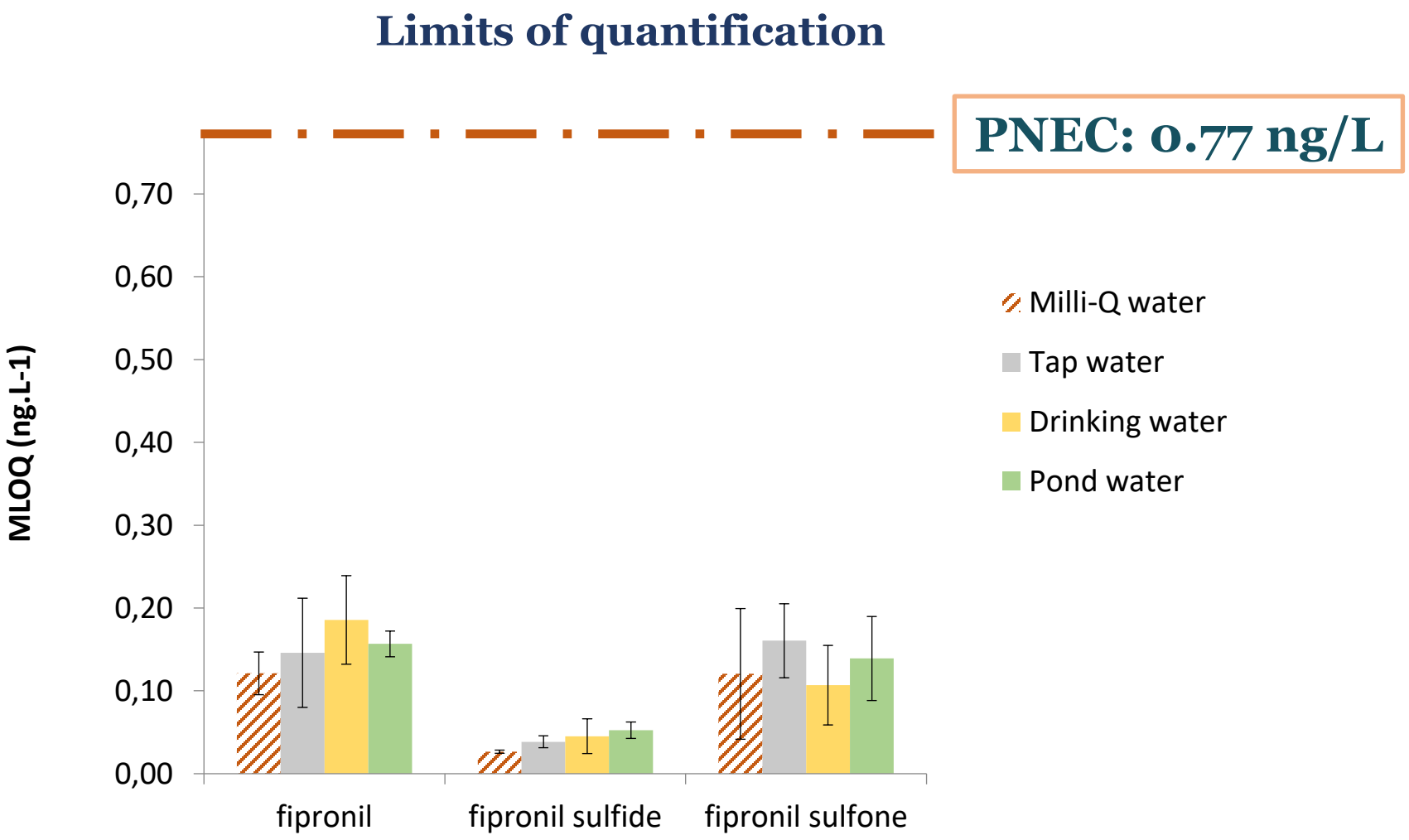
## Analysis

MS/MS detection

*MRM mode*



# Stir-Bar Desorption: method performance



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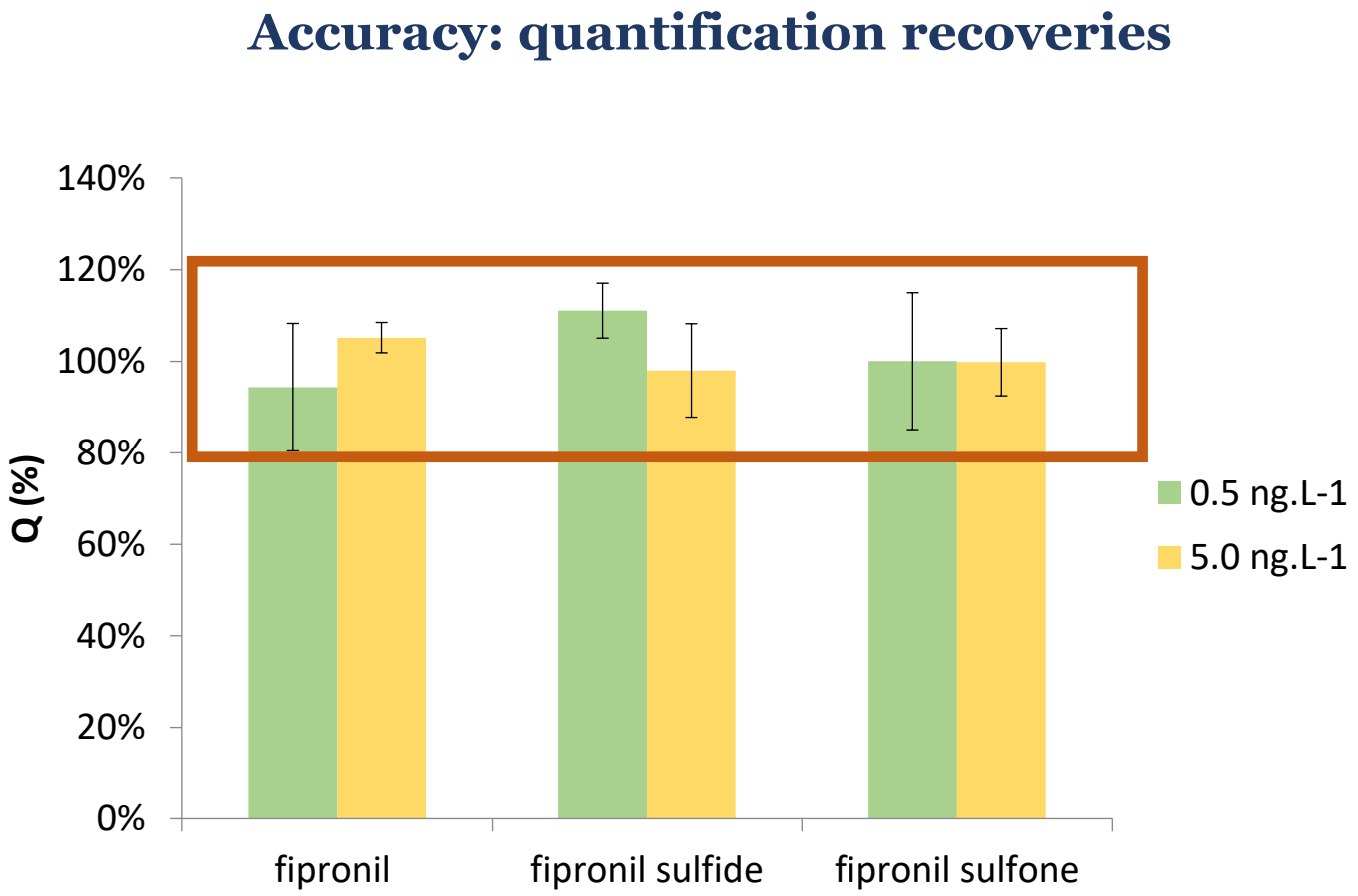
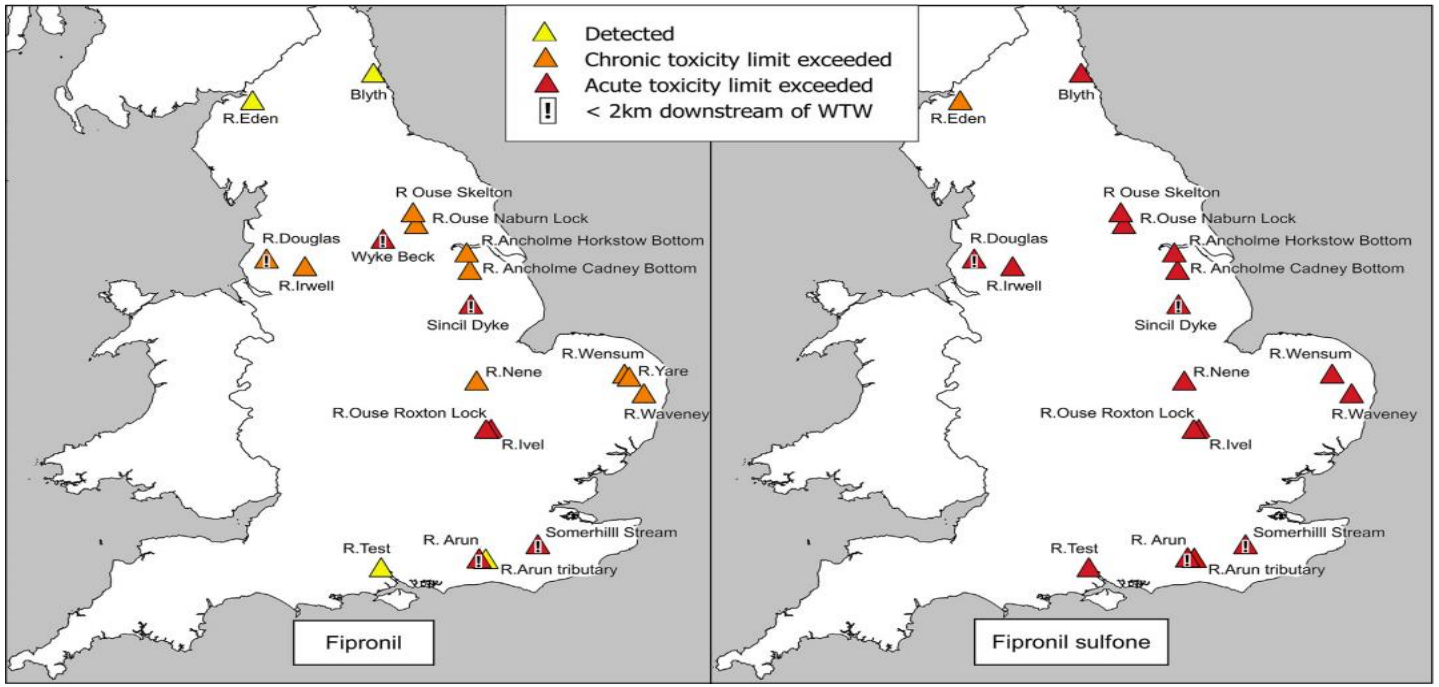


# Fipronil as a water contaminant

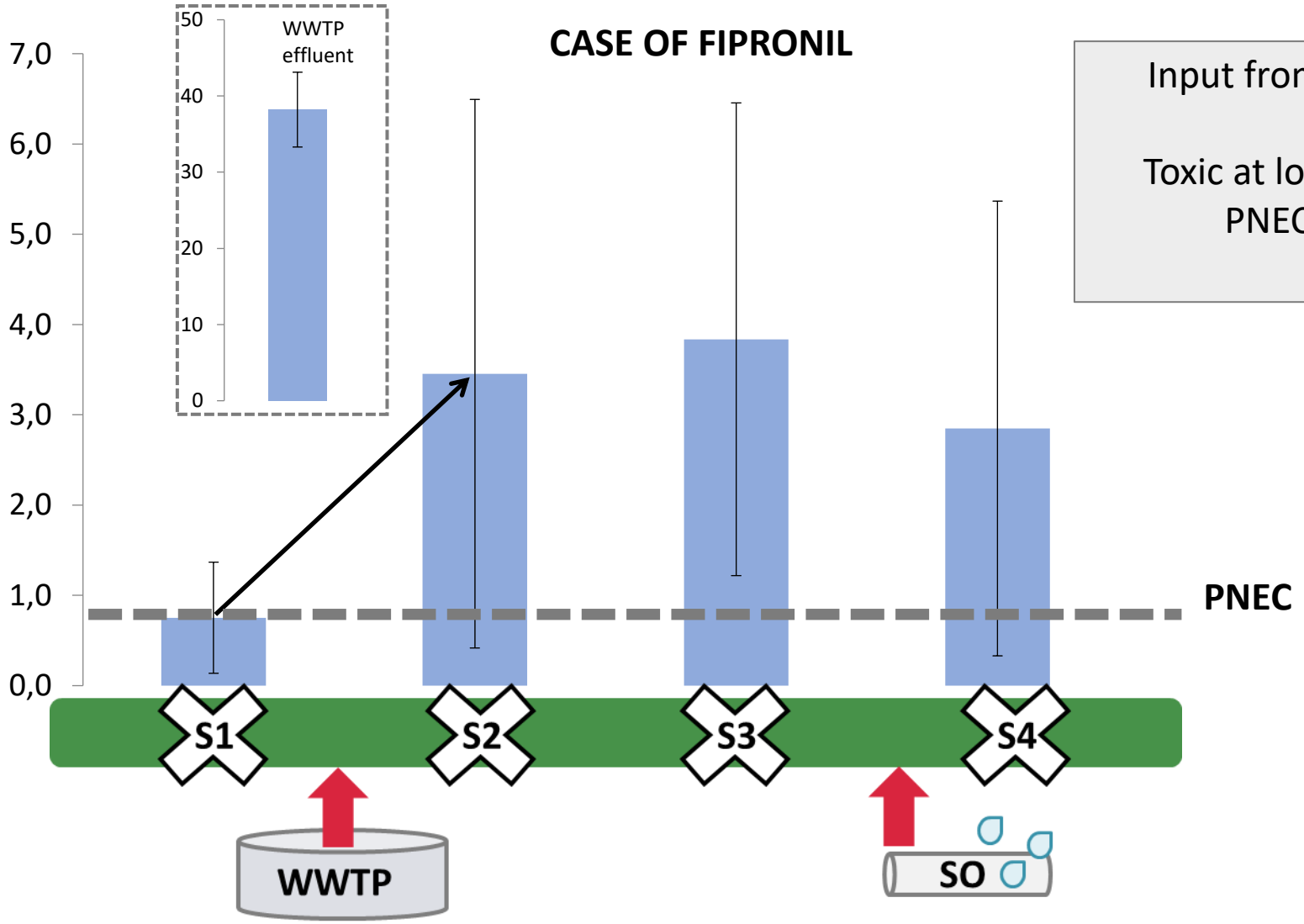
- Widespread contamination of river systems in the UK (Perkins *et al* 2021)
  - Fipronil, fipronil sulfone, fipronil sulfide and imidacloprid detected in 99%, 97%, 69% and 66% of samples, respectively
  - Mean concentrations of fipronil (17 ng/L) and fipronil sulfone (6.5 ng/L) 5.3 and 38.1 times their chronic toxicity limits of 3.2 and 0.17 ng/L, respectively.



# Jalle river contamination by fipronil

Total concentrations (ng/L) of fipronil along the continuum of the river *(dissolved phase, n=6, 2013-2015)*

(Dufour 2017)



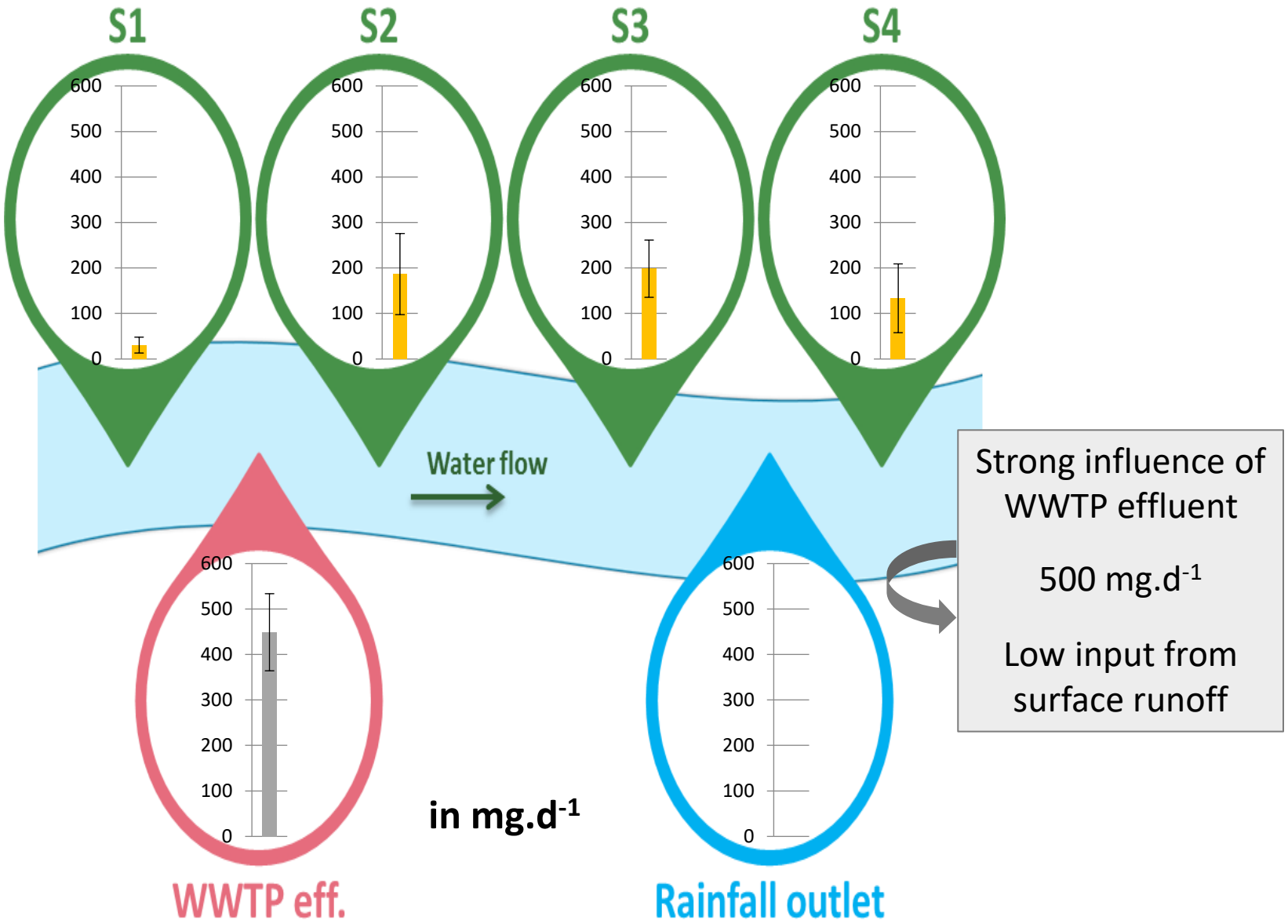

Input from WWTP effluent

Toxic at low concentrations
PNEC = 0.77 ng/L

# Jalle river contamination by fipronil

Fipronil fluxes ($mg.d^{-1}$) measured along the river (*n=6, 2013-2015)*

FLUX = [C] x flow rate

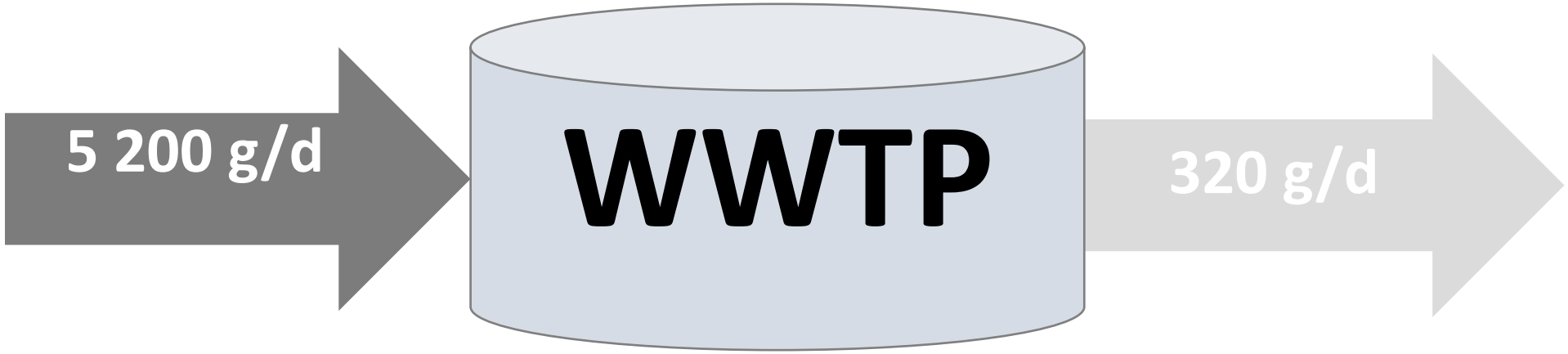



Strong influence of WWTP effluent

500 $mg.d^{-1}$

Low input from surface runoff

# Investigating sources of organic micropollutants



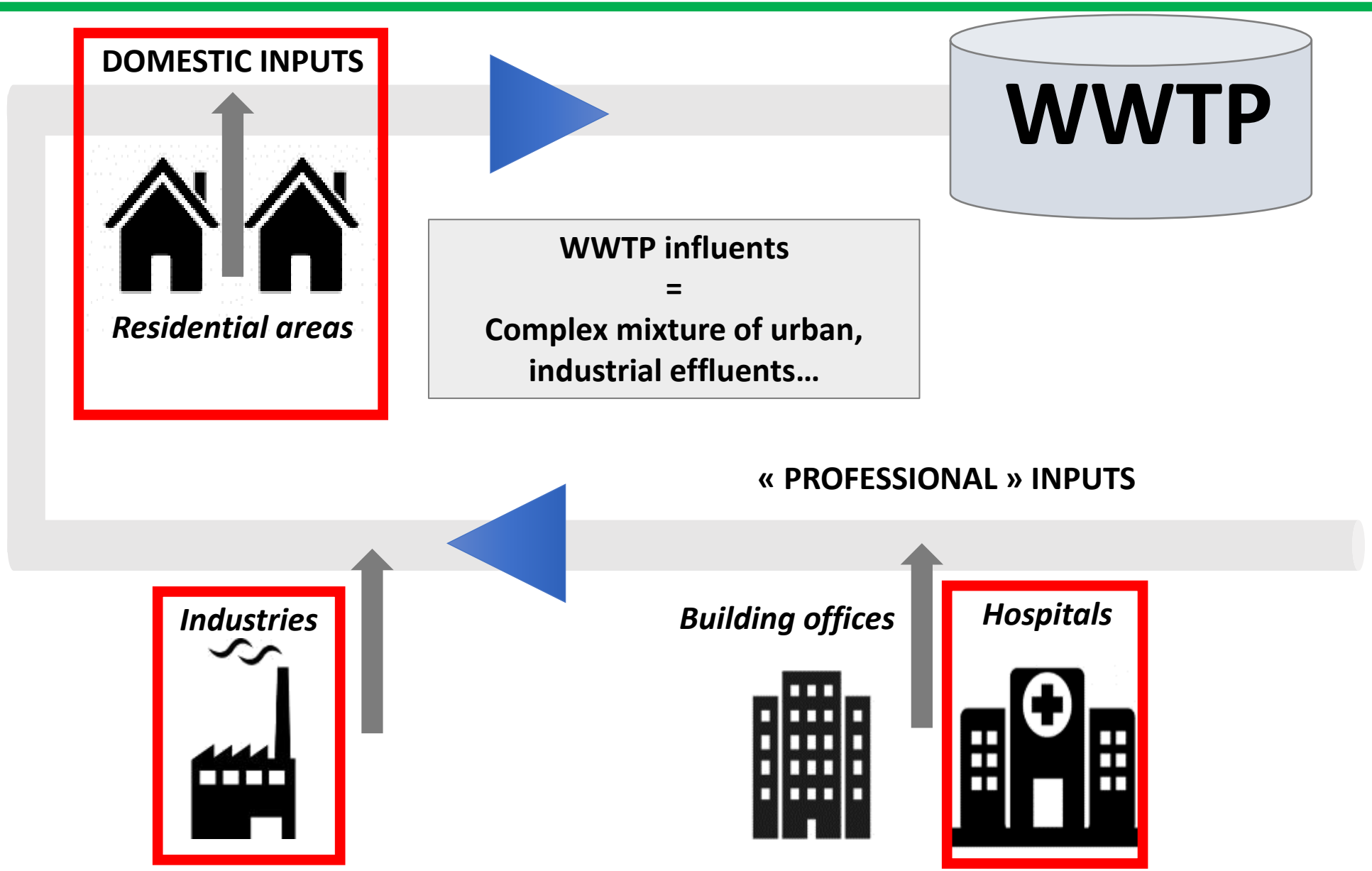

**Good removal efficiency (>90%) for most studied compounds except :**

Need to investigate the upstream of the sewage network to identify the major sources of some remanent micropollutants

Gabapentin, hydroxy-ibuprofen
AMPA, glyphosate, imidacloprid
**fipronil**…

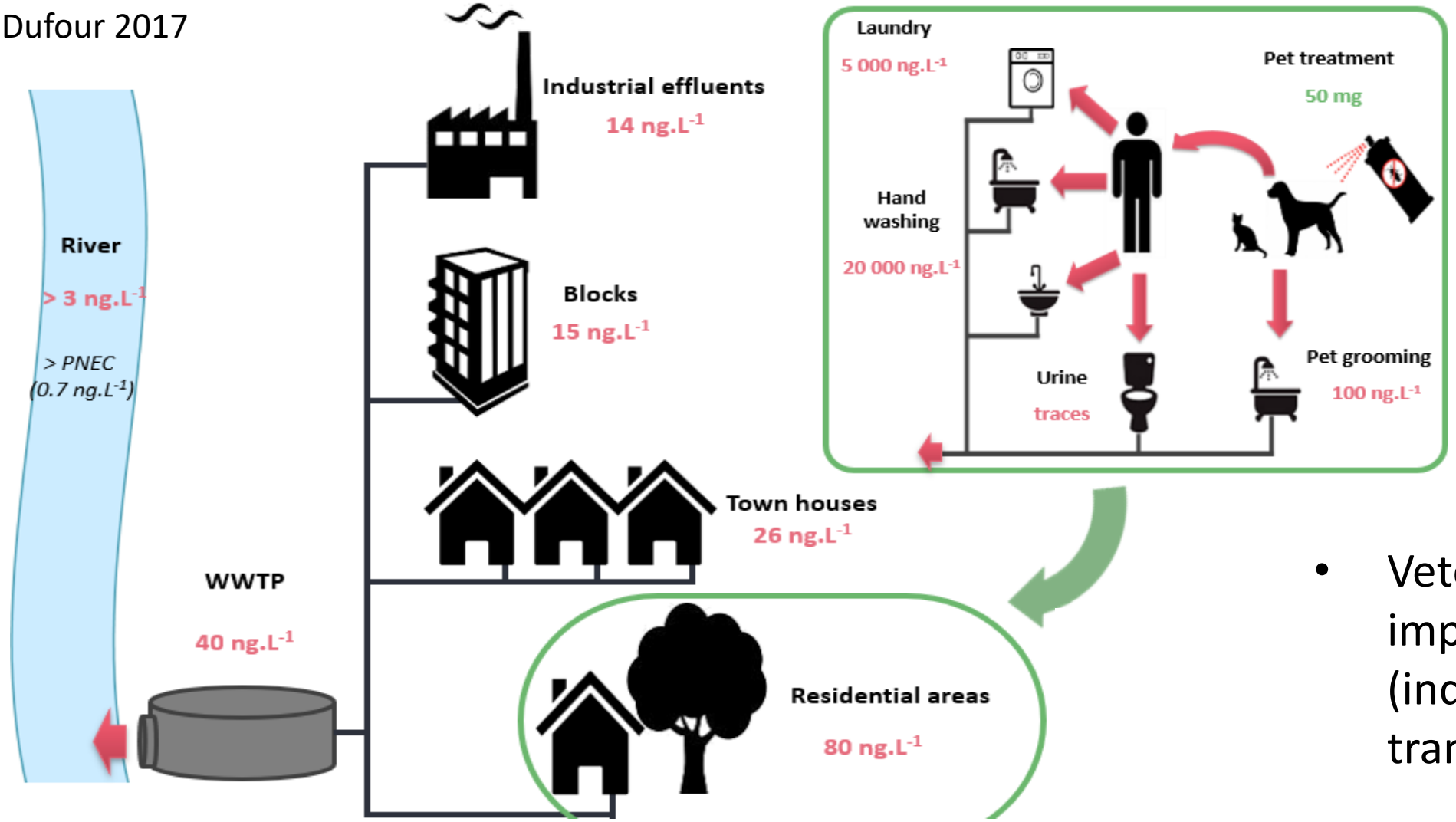
**Low level of breakdown (< 30%) for fipronil**

# Investigating sources of organic micropollutants



# Tracking the source of fipronil

Dufour 2017

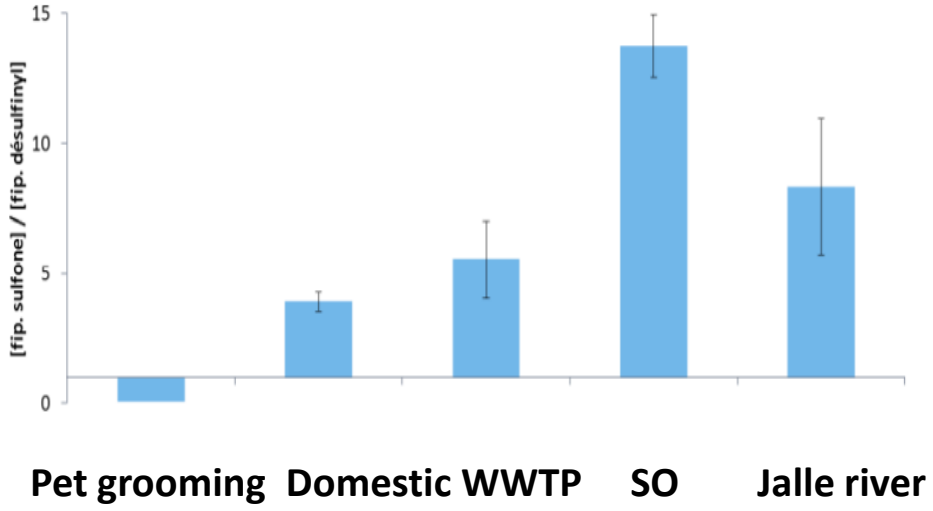


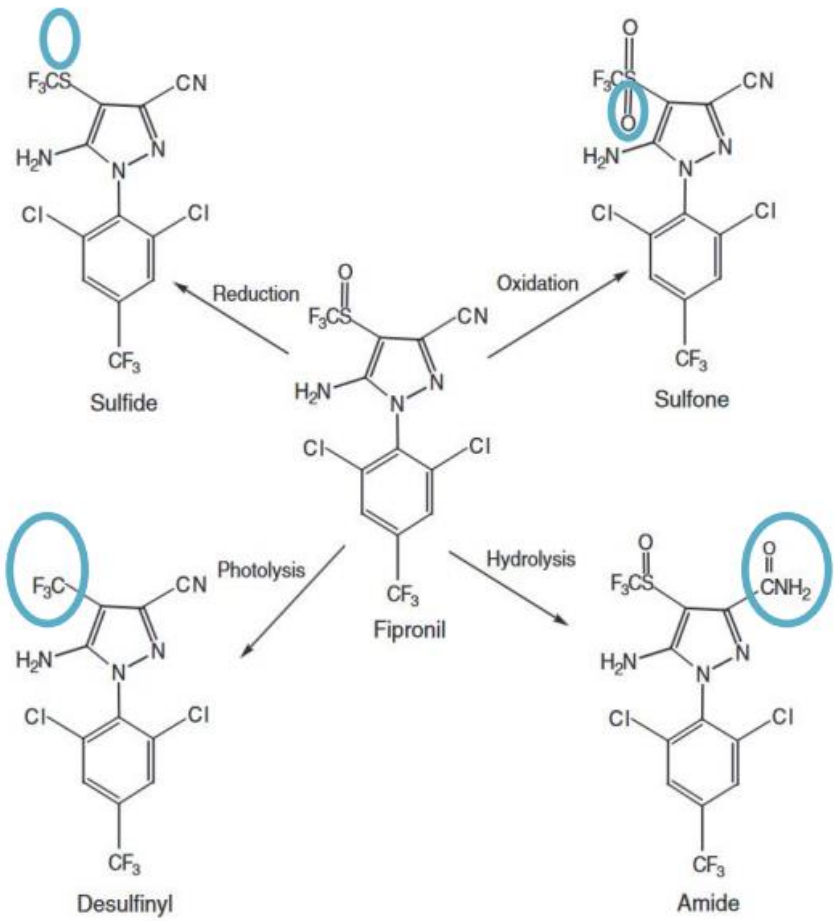

- Highest concentration in wastewater of residential areas

- Veterinary use = important source (indirect transfer > direct transfer)

# Abiotic degradation

- Fipronil sulfone / Fipronil desulfinyl variable along the wastewater system

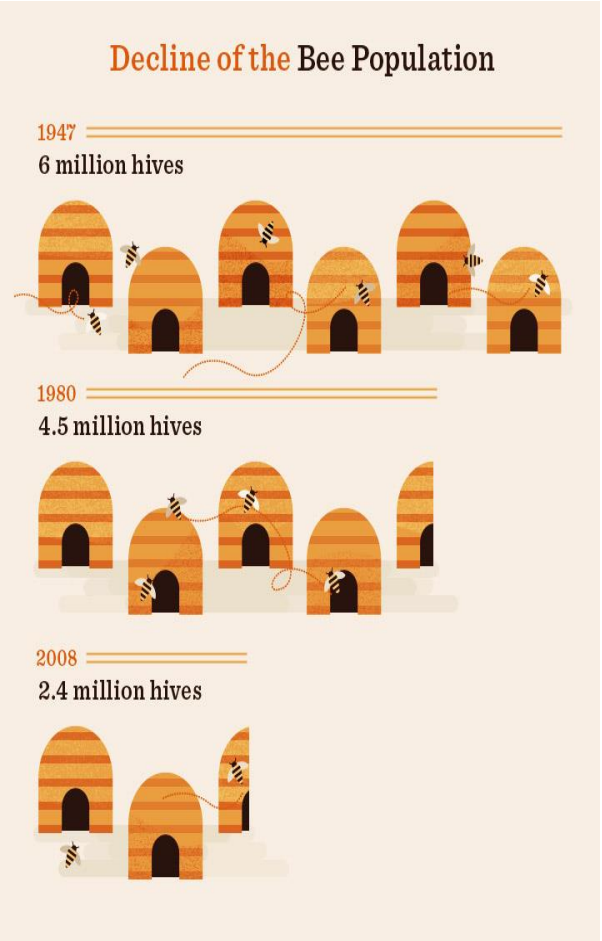



- Fipronil & its photodegradation product fipronil desulfinyl as endocrine disruptors: growth and reproduction in decapods (Goff et al, 2017)

# Toxicity of fipronil

- "Worldwide Integrated Assessment on the risks of Systemic Pesticides to Biodiversity and Ecosystems" updated recently (Pisa *et al* 2021)
- Levels of contamination of all environmental compartments frequently > LOAEC for a wide range of non-target species ⇨ serious biological and ecological impacts
- Neonicotinoids known for their role in worldwide declines of pollinator colonies



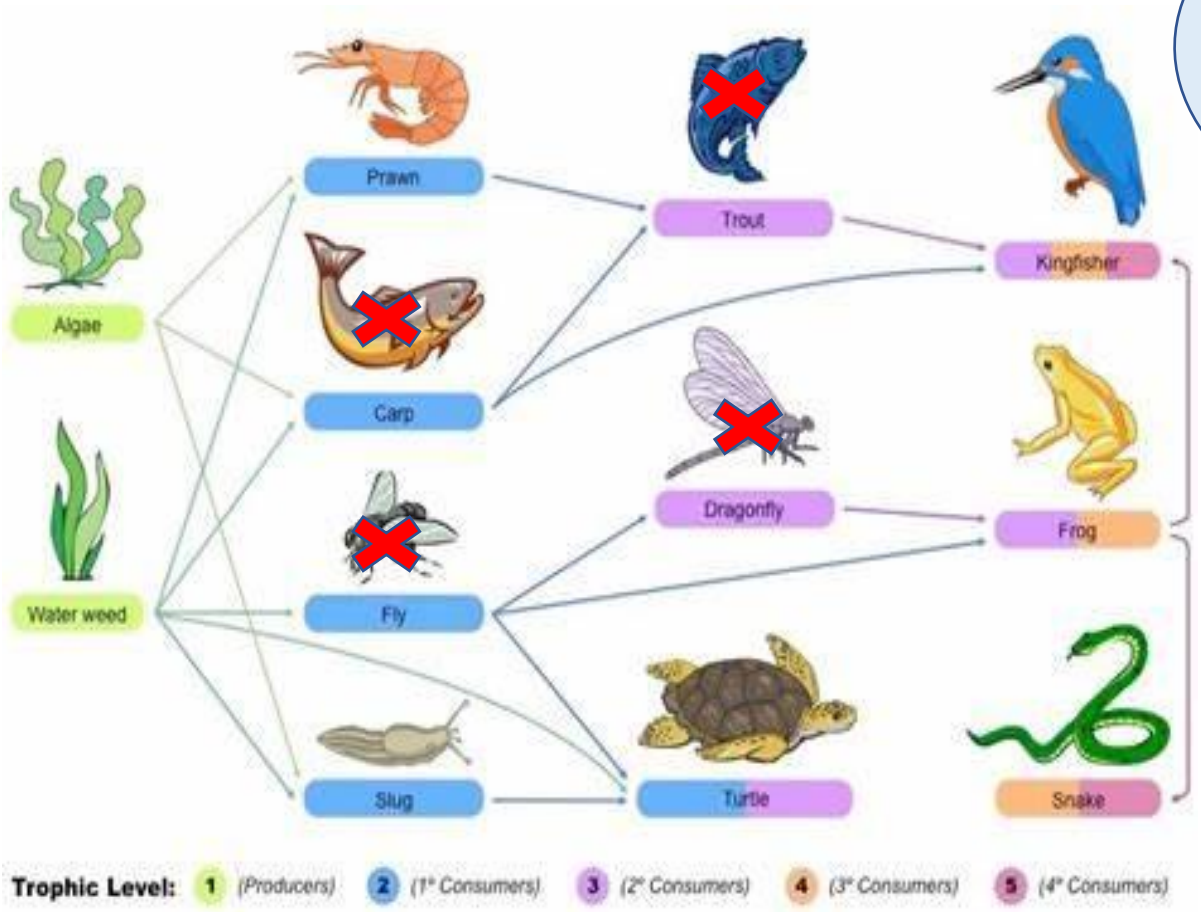
# Fipronil toxicity to invertebrates

- Treated adult bees at LD50/500: reduced motor activity, reduction in sperm viability, egg laying and larval numbers
- Significant downregulation of immunity-related genes: possible immunotoxicity
- Significant changes in invertebrate community composition after spray applications of fipronil for locust control in Queensland
- Detrimental effects on predators of pests ⇨ treatment unsuitable for integrated pest management

# Fipronil toxicity to vertebrates

- Lower affinity to vertebrate than to invertebrate GABA receptors
- Sub-lethal neurological effects in **rats**
- Effects on **bird** immunity and sometimes death due to ingestion of treated seeds
- Highly toxic to several **fish** (e.g. bluegill sunfish, Lepomis macrochirus) and some **bird** (e.g. red-legged partridge, ringnecked pheasant) species.

# Fipronil impact on ecosystems




Where is my food source gone?

- Vertebrate populations indirectly affected ⇐ depend on arthropod resources for food

# Conclusion

- Fipronil and its metabolites harmful for the environment
- Imidacloprid = neonicotinoid also used as a spot-on veterinary product (toxic to birds ingesting treated seeds)
- Pour-on, spot-on and other topical treatments = bad therapeutic practice which can be more harmful for the environment
- Should this practice be banned?
- Should the regulatory framework be strengthened?


# References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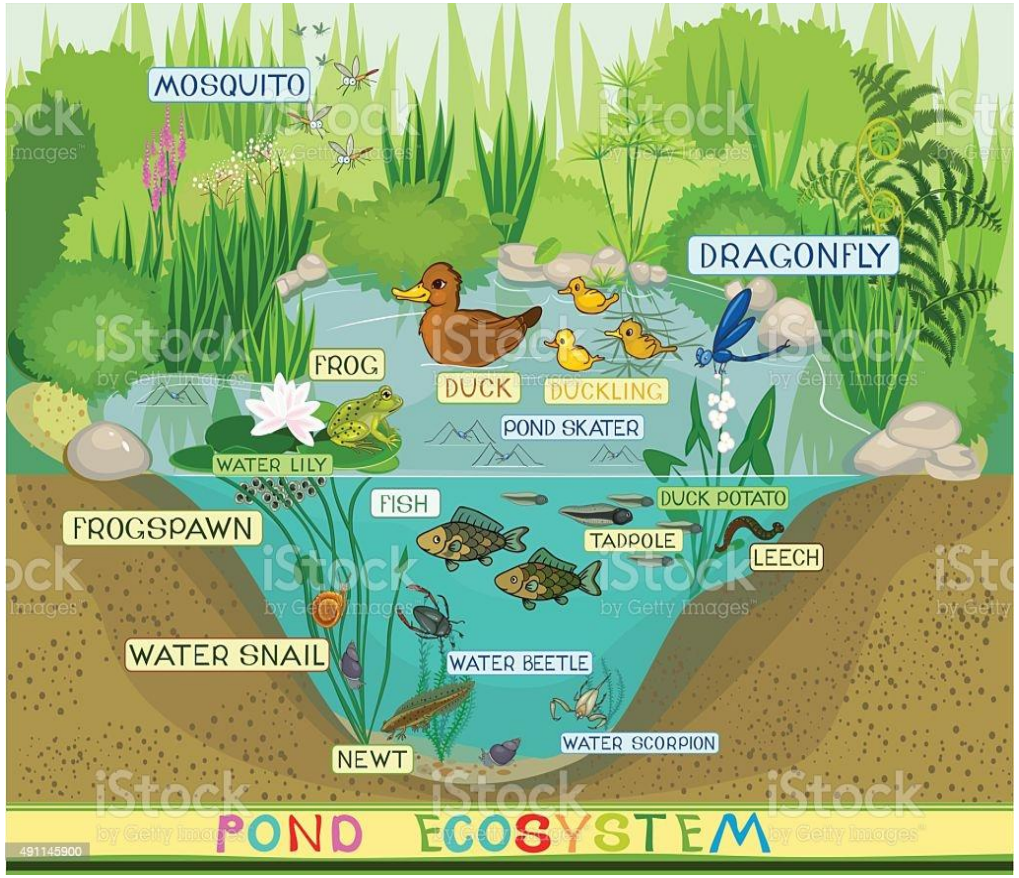
Lennard **Pisa et al** (**2021**) An update of the Worldwide Integrated Assessment (WIA) on systemic insecticides. Part 2: impacts on organisms and ecosystems. Environ Sci Pollut Res, 28, 11749-11797.

Andrew **Goff et al** (**2017**) The effects of fipronil and the photodegradation product fipronil desulfinyl on growth and gene expression in juvenile blue crabs, Callinectes sapidus, at different salinities. Aquatic toxicology, 186, 96-104.

# Thank you


MOSQUITO
DRAGONFLY
FROG
DUCK
DUCKLING
POND SKATER
WATER LILY
FISH
DUCK POTATO
FROGSPAWN
TADPOLE
LEECH
WATER SNAIL
WATER BEETLE
WATER SCORPION
NEWT
POND ECOSYSTEM


Questions Slide
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