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

- 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)

(Budzinski 2021)
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
Analysis
Gas chromatography separation

$TDU: -50 \rightarrow 280 \, ^\circ C (10 \, ^\circ C /s)$

kept 5 minutes
Fipronil detection

Analysis

MS/MS detection

MRM mode
Stir-Bar Desorption: method performance

Limits of quantification

PNEC: 0.77 ng/L

- Milli-Q water
- Tap water
- Drinking water
- Pond water

MLOQ (ng L⁻¹)

0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70

fipronil
fipronil sulfide
fipronil sulfone
Accuracy: quantification recoveries

![Bar chart showing quantification recoveries for fipronil, fipronil sulfide, and fipronil sulfone at different concentrations.](image)

**Stir-Bar Desorption: method performance**

- **Accuracy** quantification recoveries
  - 0%
  - 20%
  - 40%
  - 60%
  - 80%
  - 100%
  - 120%
  - 140%

- **Concentrations**:
  - 0.5 ng.L⁻¹
  - 5.0 ng.L⁻¹

**Q (%)**

- **fipronil**
- **fipronil sulfide**
- **fipronil sulfone**
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)

CASE OF FIPRONIL

Input from WWTP effluent

Toxic at low concentrations

PNEC = 0.77 ng/L

(Dufour 2017)
Fipronil fluxes (mg.d\(^{-1}\)) measured along the river (n=6, 2013-2015)

\[ \text{FLUX} = [C] \times \text{flow rate} \]

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

DOMESTIC INPUTS

Residential areas

WWTP influents = Complex mixture of urban, industrial effluents...

« PROFESSIONAL » INPUTS

Industries

Building offices

Hospitals
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.
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


Hélène Budzinski (2021) Course on « Sample preparation ». TACO S8, EPOC-LPTC, Master EXCE, University of Bordeaux.


Thank you