# From Source to Tap : Tracing back the origins of 1,2,4-Triazole in Belgian Drinking Water

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De Watergroep

VLAAMSE MILIEUMAATSCHAPPIJ

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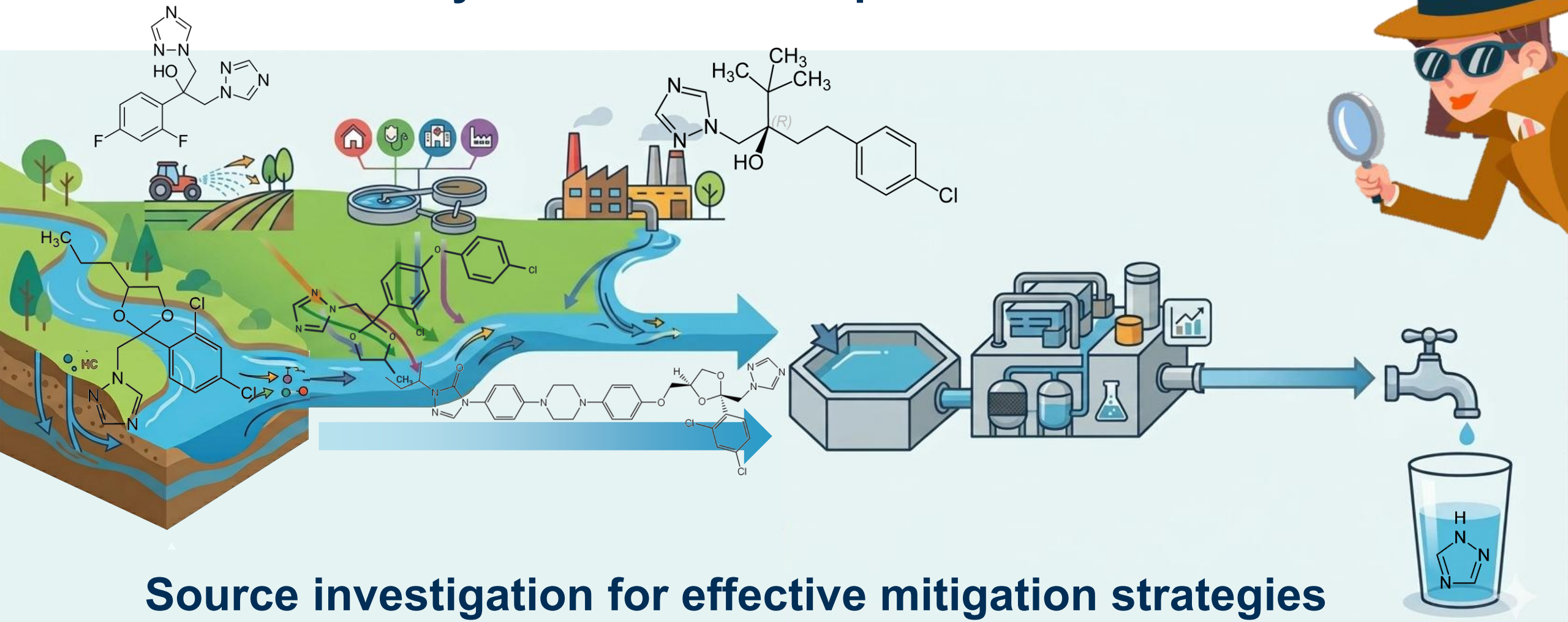
# What if we only measure the endpoint?

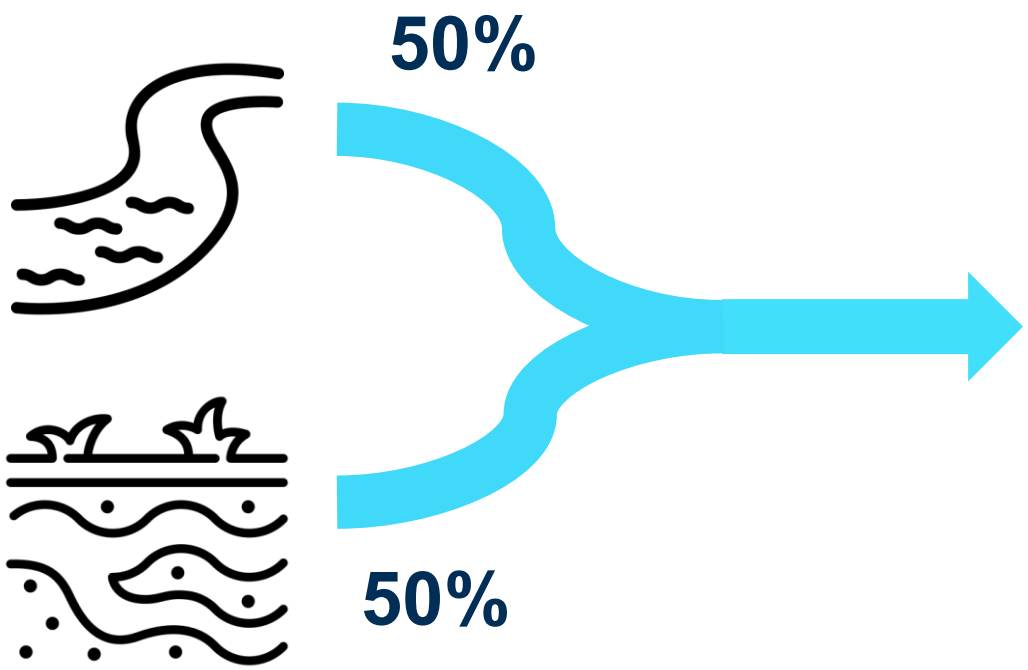


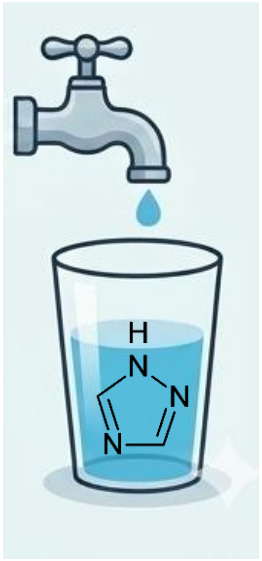
## Source investigation for effective mitigation strategies

# Surface water is extra vulnerable to contamination

## Flanders

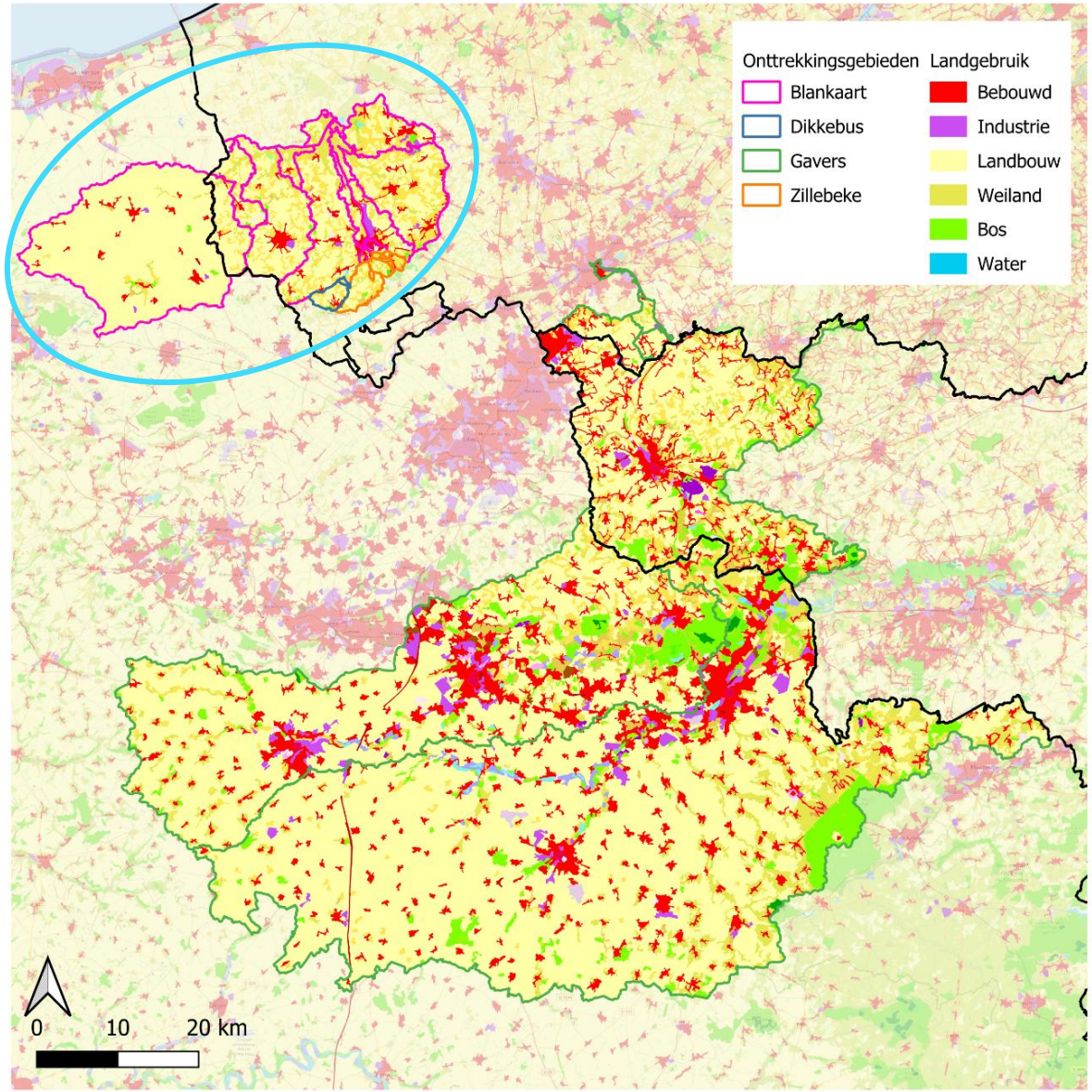
## Drinking water sources




**1,2,4-Triazole**

# Extraction areas drinking water from surface water



# Source investigation: multi-method approach

1. Identification of potential sources 1,2,4-Triazole: Literature

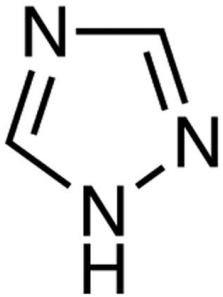
2. Pathways to surface water

3. Spatial analysis of potential sources
   - Modelling diffuse agricultural inputs
   - Mapping point sources

4. Analysis monitoring data
   - Time-series analysis
   - Non-Target Analysis

# 1. Identification of potential sources

## 1,2,4-triazole = building block of fungicides




1. Pesticides: break down to 1,2,4-triazole in soil or water + authorized use
   - Biocides tebuconazole and propiconazole for wood protection (industrial treatment, limited for exterior housing)
   - Plant Protection Products 10 potential mother compounds

     Wide authorized use!

| Werkzame stof | Verkoop BE 2023 (kg) | Aantal producten | Aardappelen + pootgoedteelt | Sierplanten Sierbomen | Granen (winter + zomer) | Bieten (suiker + voeder) | Koolzaad (winter + zomer) | Groenten - kolen | Groenten -vruchtgewassen | Groenten - knolgewassen | Groenten - bladgroenten | Groenten - overige | Kruiden | Fruit | Fruitbomen | Gazons + Golferreinen | Bosbouw |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Amisulbrom | 5.074 | 6 | x | x | | | | | | | | | | | | | |
| Bromuconazole | 2.244 | 2 | | | x | | | | | | | | | | | | |
| Difenoconazole | 25.716 | 37 | x | x | x | x | x | x | x | x | x | x | x | x | x | | |
| Mefentrifluconazole | 21.553 | 15 | x | | x | x | x | | x | | | | | x | x | | |
| Metconazole | 3.860 | 20 | | x | x | x | x | | | | | x | | | | x | |
| Paclobutrazol | 6 | 2 | | x | | | | | | | | | | | | | |
| Penconazole | 608 | 3 | | x | | | | | x | | | | | x | x | | |
| Prothioconazole | 62.885 | 93 | x | | x | x | x | x | | x | | | | | | | |
| Tebuconazole | 33.329 | 29 | | x | x | | x | x | x | x | | x | | | x | | x |
| Tetraconazole | 3.502 | 9 | | x | x | x | | | | | | x | | | | | x |

# 1. Identification of potential sources

## 1,2,4-triazole = building block of fungicides

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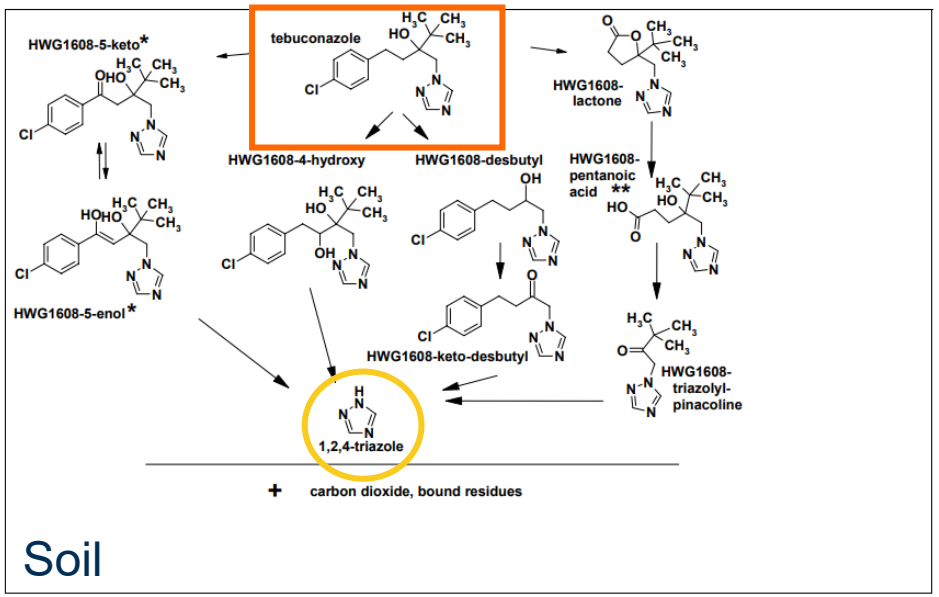
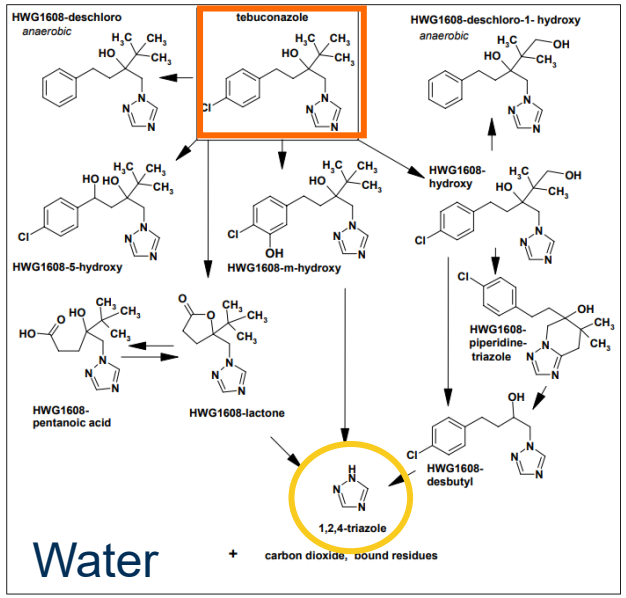
**Complex breakdown mechanisms with formation of intermediary products**




**Parent compound**

≠ intermediary products

**Final breakdown product: 1,2,4-triazole**

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# 1. Identification of potential sources

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2. Pharmaceuticals
   - Human use fluconazole and itraconazole, primary care + hospitals

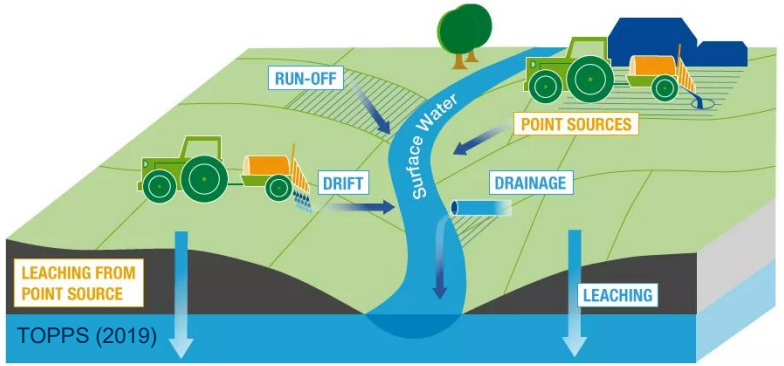
3. Industrial discharges
   - Proces water of companies wood treatment, food processing

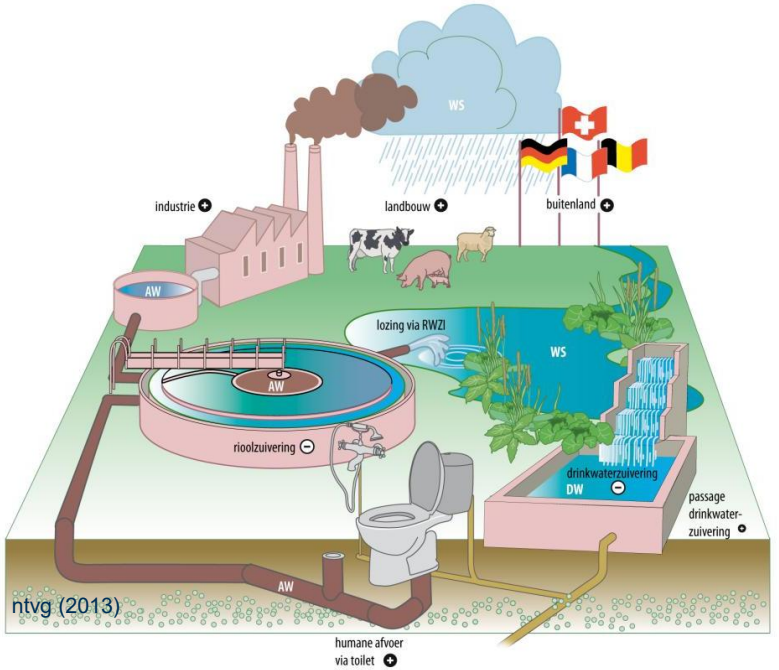
# 2. Pathways to surface water

1. Plant protection products
   - Diffuse
     - Spray drift
     - Surface runoff and erosion
     - Drainage ~~+ groundwater~~
   - Point sources

2. Pharmaceuticals – Human use
   - Wastewater treatment plants (WWTP's)
   - Untreated household wastewater

3. Industrial discharges (food processing + wood treatment)
   - Direct discharge into surface water
   - Waste water treatment plants (WWTP's)



# 3. Spatial analysis of potential sources

## Diffuse inputs from Plant Protection Products

**GOAL:** Theoretical estimate of amount of 1,2,4-triazole to surface water

- Spatial pressure patterns
- Contributions per crop group

**DATA:**

- Selection of 10 mother compounds
  - Maximum authorized use (Belgium: Fytoweb, France: E-Phy)
  - Chemical properties: DT50, metabolization fraction in soil and water (EFSA-conclusion reports)
- Agricultural land use 2023 at parcel level (Flanders: Geopunt, Wallonia: WallonMap, France)

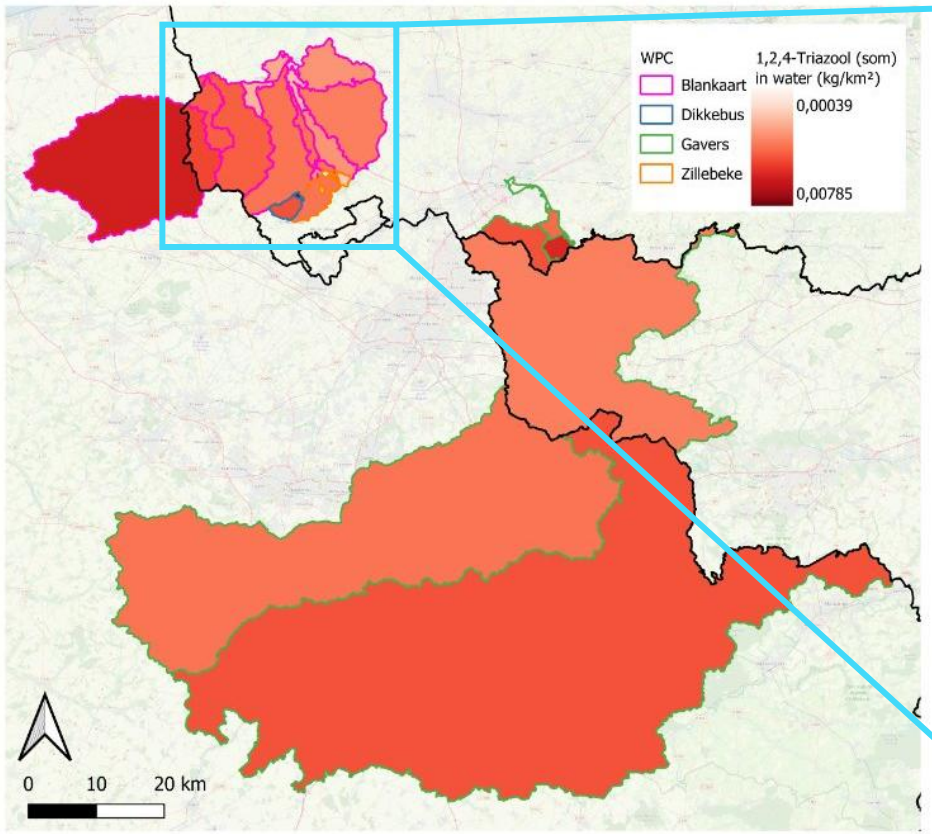
**METHOD:**

- Conservative estimates based on FOCUS STEP 1- surface water: erosion + drainage
- Total input = Sum of input from 10 mother compounds scaled for sales 2023 (BE and FR)

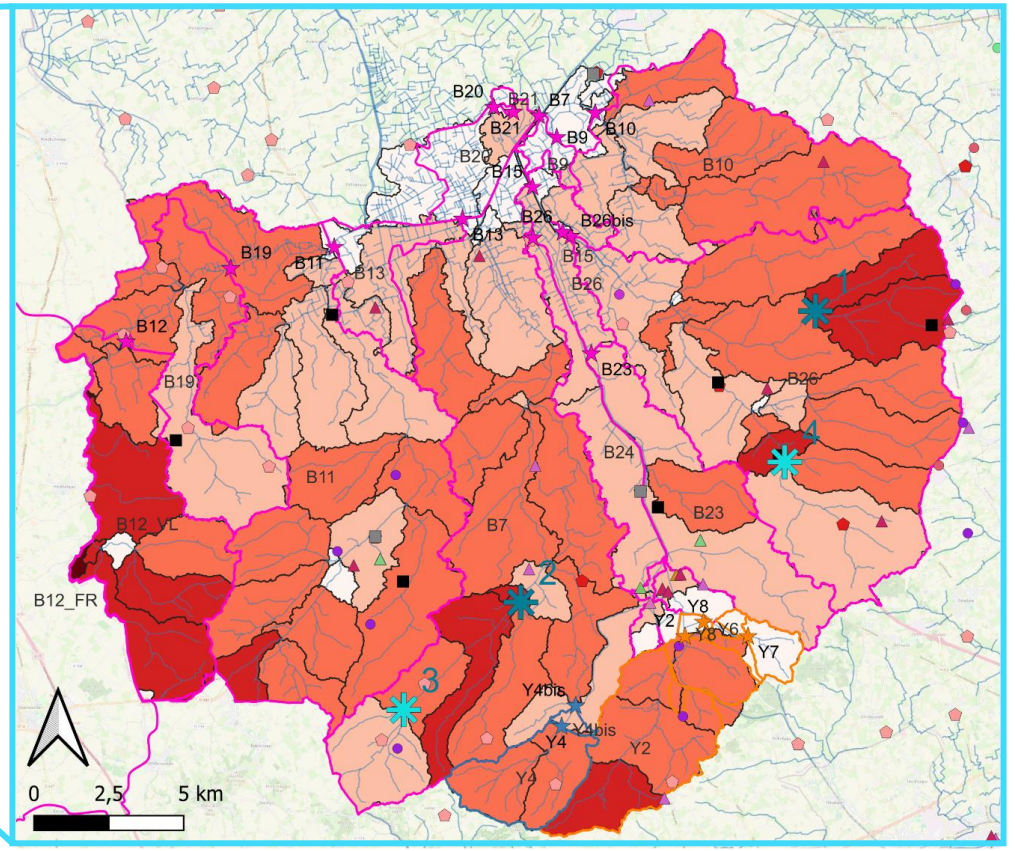
# 3. Spatial analysis of potential sources

## Diffuse inputs from **Plant Protection Products**: Spatial pressure patterns

### Current monitoring network




### New monitoring locations



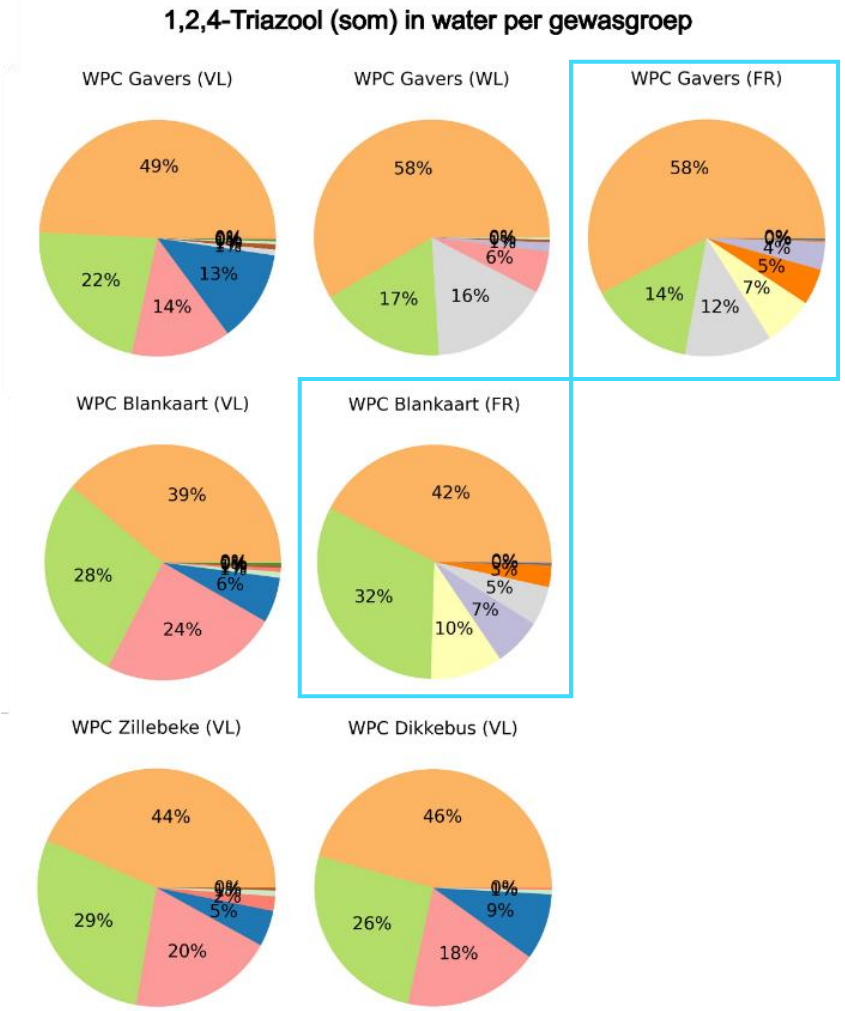
# 3. Spatial analysis of potential sources

## Diffuse inputs from **Plant Protection Products**: Contributions per crop group

Majority of theoretical contributions from:

1. Grains
2. Potatoes
3. Vegetables

France: also corn



# 3. Spatial analysis of potential sources

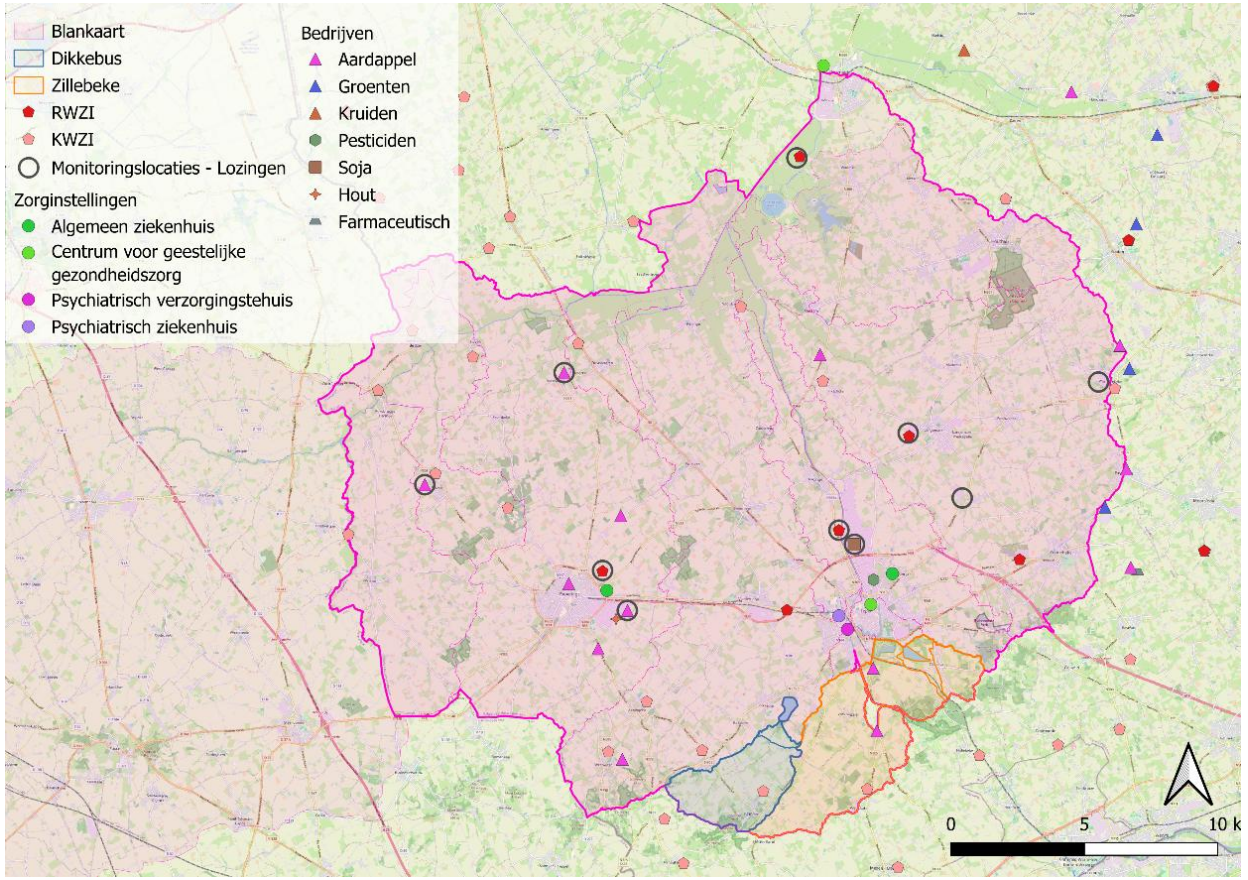
## Point sources: Pharmaceuticals and industrial discharges

**Mapped for extraction areas:**

- Pharmaceuticals:
  - Healthcare facilities
  - WWTP's

- Industrial discharges:

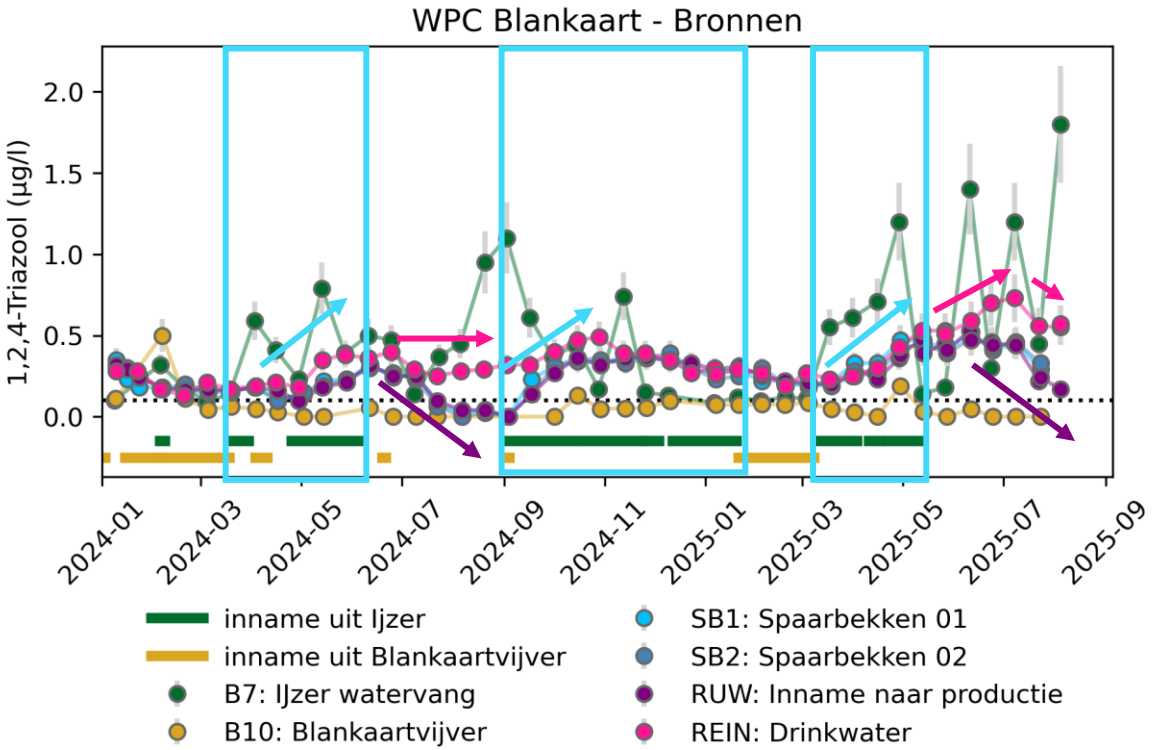
  Companies with
  - Food processing
  - Wood treatment
  - Pharmaceutical manufacturing
  - Pesticide manufacturing



# 4. Analysis monitoring data

## WPC Blankaart: **Sources** and **variation during drinking water production**

- 2 sources: IJzer en Blankaartvijver
  - Blankaartvijver: usually <0,1 µg/l
  - IJzer: high concentrations up to 3 µg/l, always > 0,1µg/l



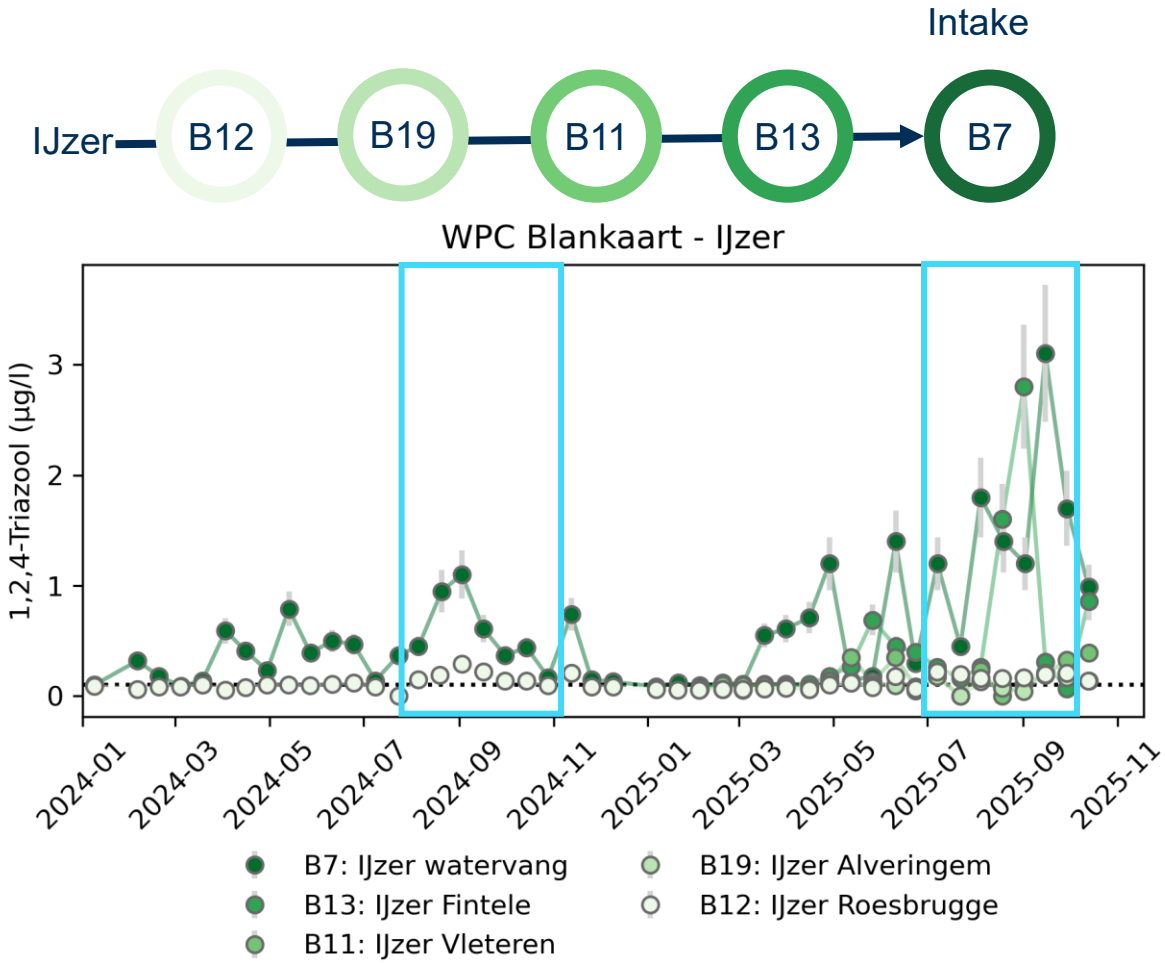
# 4. Analysis monitoring data

## WPC Blankaart – variation along river IJzer

Measurements along river IJzer:

- B12 – border FR:
  - Concentrations around 0,1 µg/l
  - > 0,1 µg/l: July – October

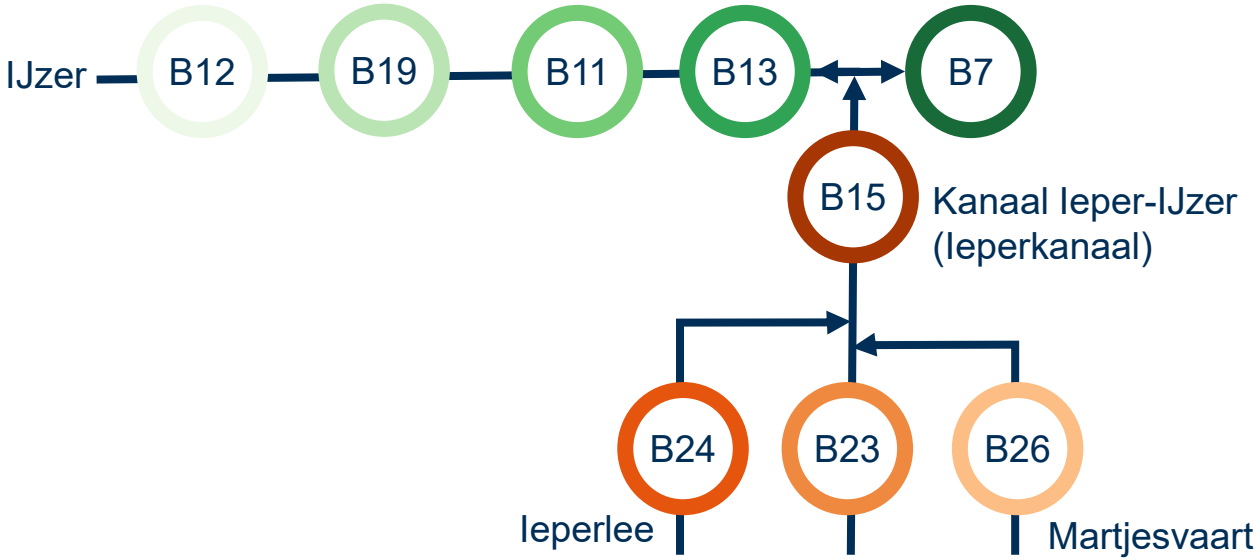
- B7: intake
  - Spring + summer: strong fluctuations in concentration ~ flow direction water
  - Concentrations high when low in all upstream locations

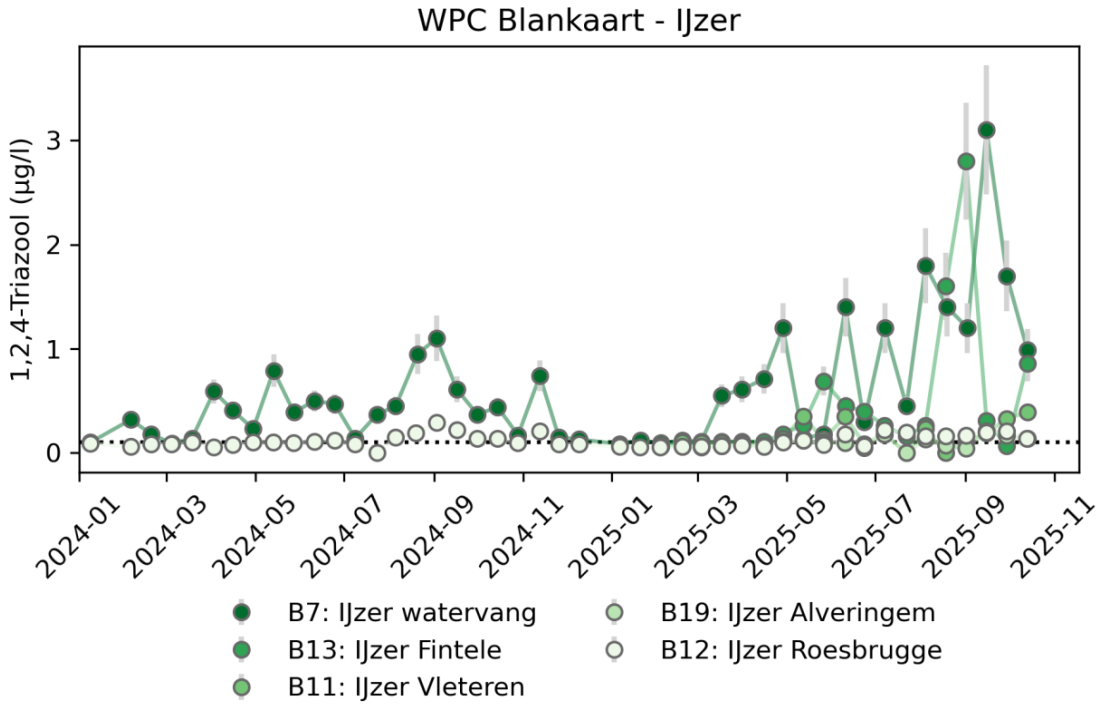


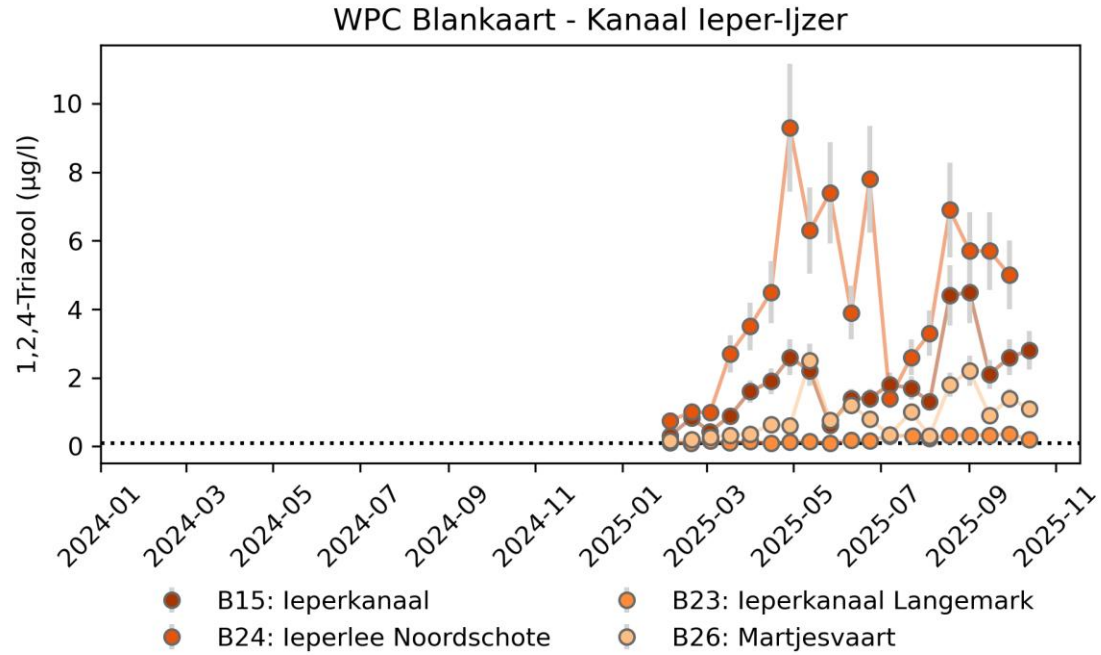
# 4. Analysis monitoring data

## Variations along IJzer – Canal Ieper-IJzer

- Strong increase in concentrations IJzer after inlet Ieperkanaal
- High concentrations canal Ieper-IJzer, dominated by very high concentrations Ieperlee
- Linked to industrial discharges: industry + WWTP



# 4. Analysis monitoring data

## Contributions from discharges

**Discharges**:

- Different companies and Waste Water Treatment Plant (WWTP) direct discharge on Ieperlee + canal
- 3 measurement campaigns
  - 124T Industrial discharges: 0,2 – 32 µg /l
  - 124T WWTP effluent: 0,2 – 1,1 µg/l
    - Detection of *propiconazole (biocide)*
  - 124T wastewater hospital: 0,2 µg/l

Discharges have a dominant contribution to the high concentrations of 1,2,4-triazole in the IJzer river at the drinking water intake point

# 4. Analysis monitoring data

## Non-target analysis

- Not all mother compounds measured with standard analysis
- Measured mother compound intake (*tebuconale)* cannot explain increase in 1,2,4-triazole concentrations during drinking water production

    -> Non-target analysis 1,2,4-triazole containing compounds in raw water

| m/z meas. | Name | Molecular Formula | area |
|---|---|---|---|
| 320.15313 | Metconazole | C17H22ClN3O | 4086 |
| 334.16948 | (1R,2S,5R)-2-(4-chlorobenzyl)-5-isopropyl-1- (1H-1,2,4-triazol-1-ylmethyl)cyclopentanol | C18H24ClN3O | 4708 |
| 318.13769 | (5E)-5-[(4-chlorophenyl)methylidene]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol | C17H20ClN3O | 10434 |
| 406.07291 | 1-[[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole | C19H17Cl2N3O3 | 8328 |
| 292.12168 | cyproconazole | C15H18ClN3O | 2862 |
| 308.15278 | Tebuconazole | C16H22ClN3O | 8790 |
| 318.09993 | triadimenol | C14H18ClN3O2 | 1130 |
| 307.11323 | Fluconazole | C13H12F2N6O | 8356 |

(breakdown products)
Plant protection products

Pharmaceutical

# Source investigation De Blankaart

## Summary

- Elevated concentrations of 1,2,4-triazole in drinking water (max 0,7 µg/l)
- Dominant contribution from discharges (WWTP + industry)
- 1,2,4-triazole originates from multiple sources:
  - Discharges industry and WWTP
    - biocide, pharmaceutical and (breakdown products) of plant protection products
  - Agriculture
    - (breakdown products) plant protection products

# Conclusion

- Multi-method source investigation framework:
  - Literature review
  - Spatial mapping and modelling
  - Targeted monitoring
  - Advanced analytical techniques: Non-Target Analysis

- Approach
  - support regulatory exposure assessment for proactive risk management
  - enables water utilities to prioritize interventions
  - Transferable to other contaminants of emerging concern

# Questions or opportunities?

## Get in touch!

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