

Leaching of unexpected cyazofamid degradation products into groundwater demonstrates gaps in current pesticide risk assessment

— Results from the Pesticide Leaching Assessment Programme (PLAP)

Nora Badawi¹, Sachin Karan¹, Eline B. Haarder¹, Ulla E. Bollmann¹, Christian N. Albers¹ and Kirsten Kørup²

LuWQ

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PLAP

www.plap.dk



GEUS

¹Geological Survey of Denmark and Greenland (GEUS), Oester Voldgade 10, DK 1350, Denmark

²Department of Agroecology, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark

What is the Pesticide Leaching Assessment Programme (PLAP)?

- National monitoring programme functioning since 1999
- Funded by the Danish Government via the Pesticide Strategy 2022-2026
- Collaboration between the Danish EPA (owner), GEUS (project lead) and Aarhus University (Dept. AGRO and ECOS)
- Aimed at evaluating the leaching risk of pesticides and/or their degradation products to young groundwater under field conditions



PLAP - objective

1) Evaluate whether approved pesticides and their degradation products will leach to the ground water in concentrations exceeding the limit value of 0.1 µg/L for groundwater

- ✓ pesticides applied in accordance with current regulations
- ✓ maximum permitted dosages according to crop and BBCH stages
- ✓ actual Danish field conditions

2) Improve the scientific foundation for decision-making in the Danish regulation of pesticides by enabling field studies to be included in the risk assessment of selected pesticides

PLAP fields – Location

PLAP fields represent differences in climate and geology

Field sizes:

- 1,1 - 2,1 ha

Field types:

- 4 clay till fields (1 on standby)
- 2 sandy fields (1 on standby)

Agricultural management:

- Conventional cropping
- Pesticides
- Fertilizer

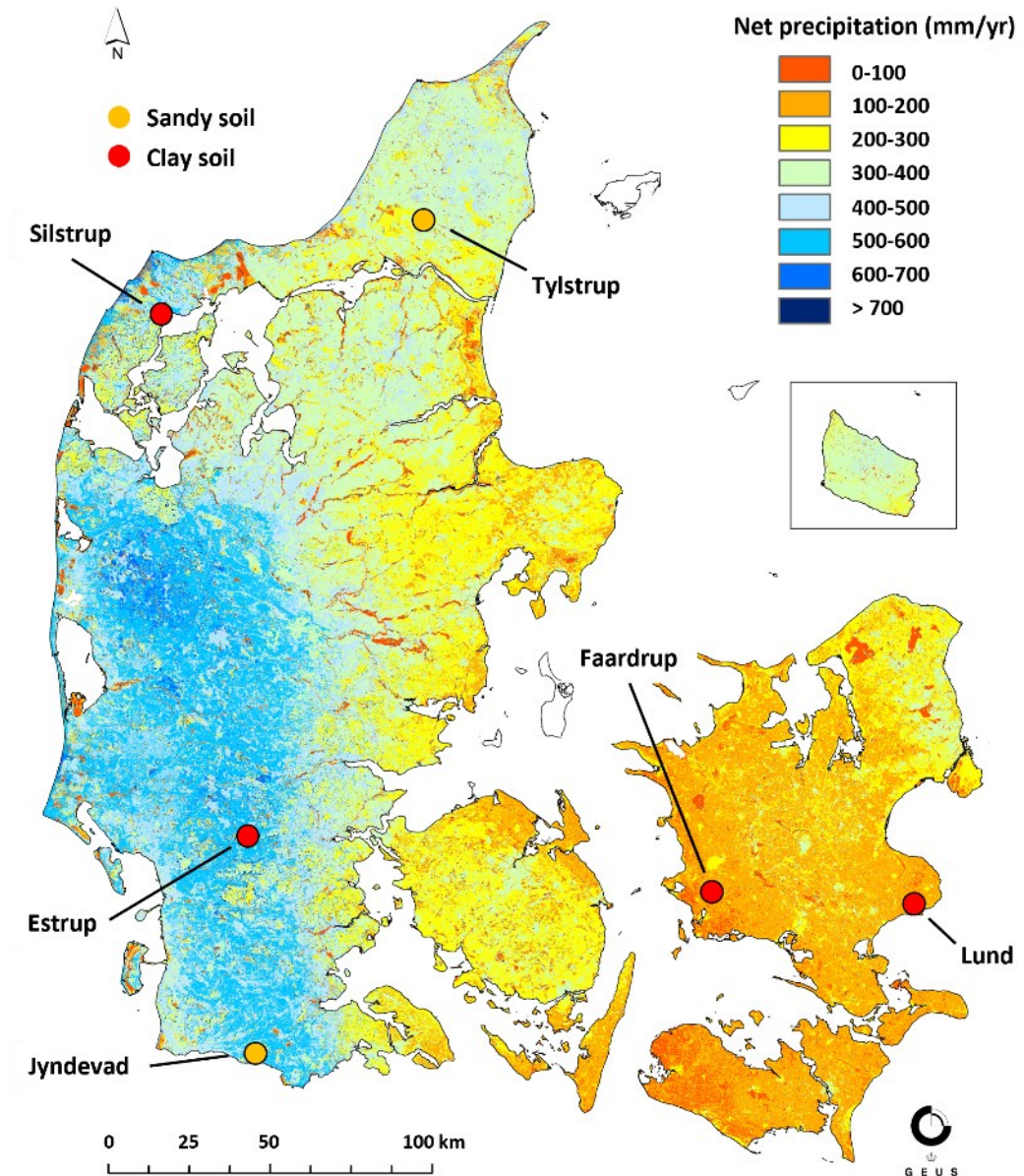


Figure 1. Annual net precipitation across Denmark 1990-2019 (Henriksen et al., 2021)

PLAP Fields - Installations

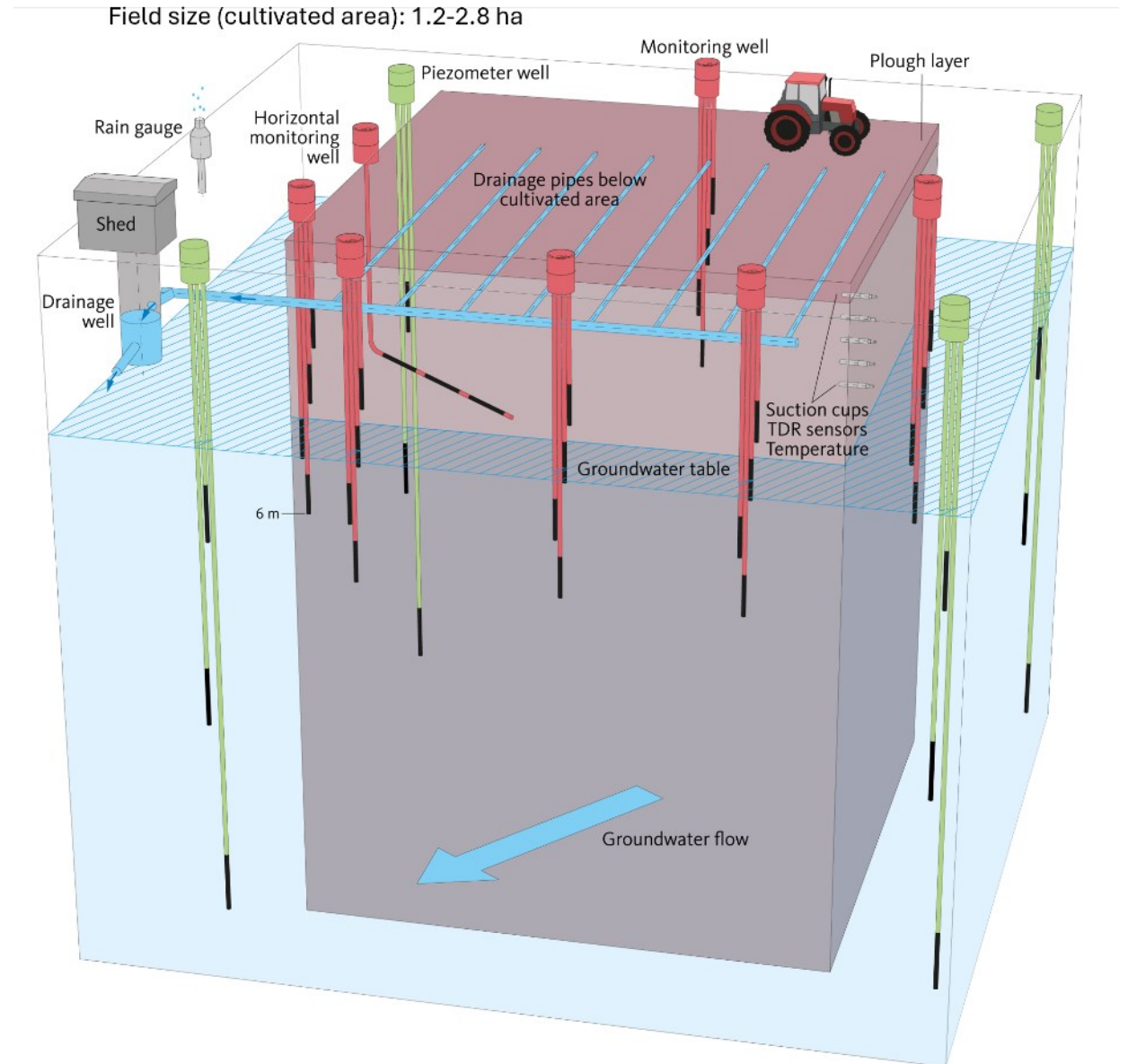
Unsaturated zone:

- S1 og S2 – suction cups (1 mbgs, sandy fields)
- **Drainage system** - (1 mbgs, clay till fields)

Saturated zone:

- **M1-7** – vertical groundwater wells (1.5-5.5 mbgs)
- **H1-3** - horizontal groundwater wells (2.0/3.5 mbgs)

- **P1-4** – groundwater wells for groundwater level measurements (2-12 mbgs)



PLAP Fields - monitoring

Monthly:

Analysis of samples from groundwater + unsaturated zone (sandy fields):

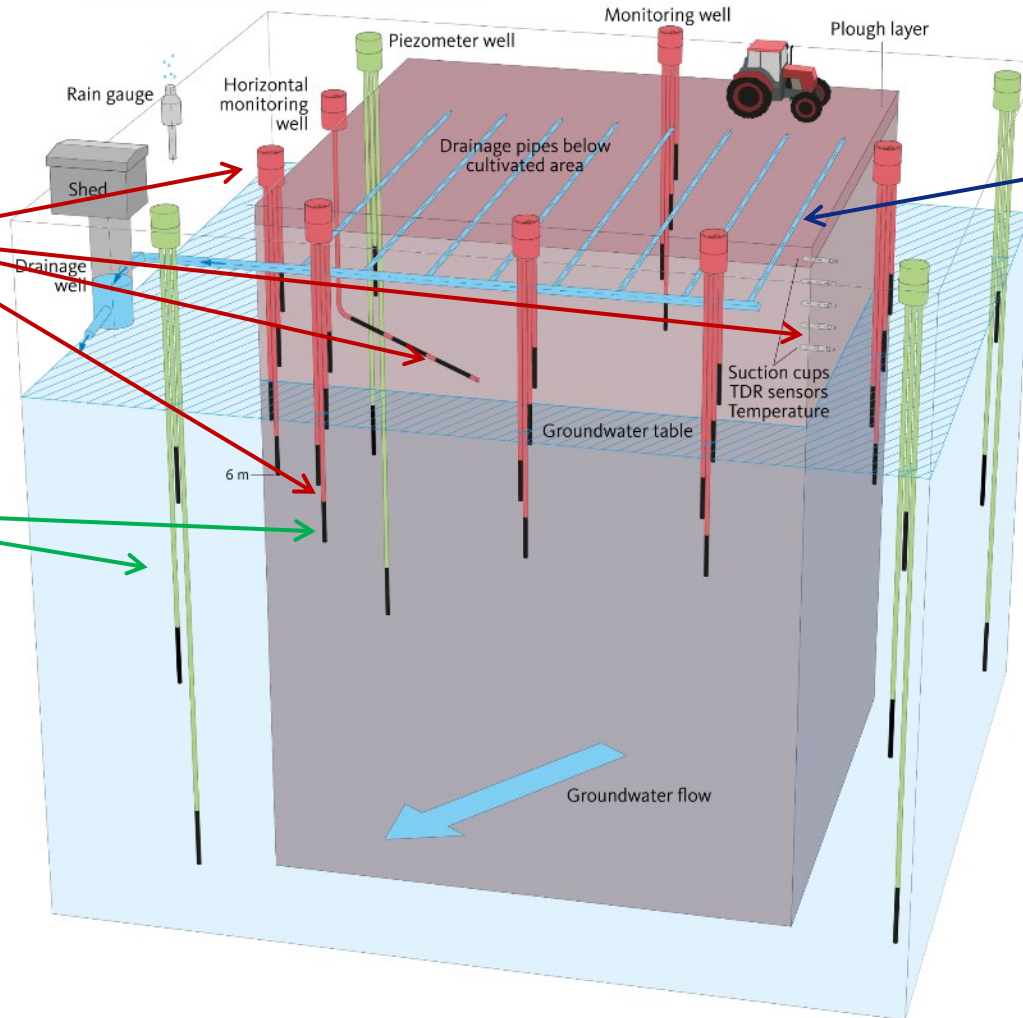
- Pesticides/TP's
- Inorganics (nitrate)

Measurement of groundwater level:

- All wells



Field size (cultivated area): 1.2-2.8 ha



Weekly:

Analysis of drainage (and groundwater – new tests):

- Pesticides/TP's
- Inorganics (pt nitrate)

PLAP Fields - monitoring

Monthly:

Analysis of samples from groundwater + unsaturated zone (sandy fields):

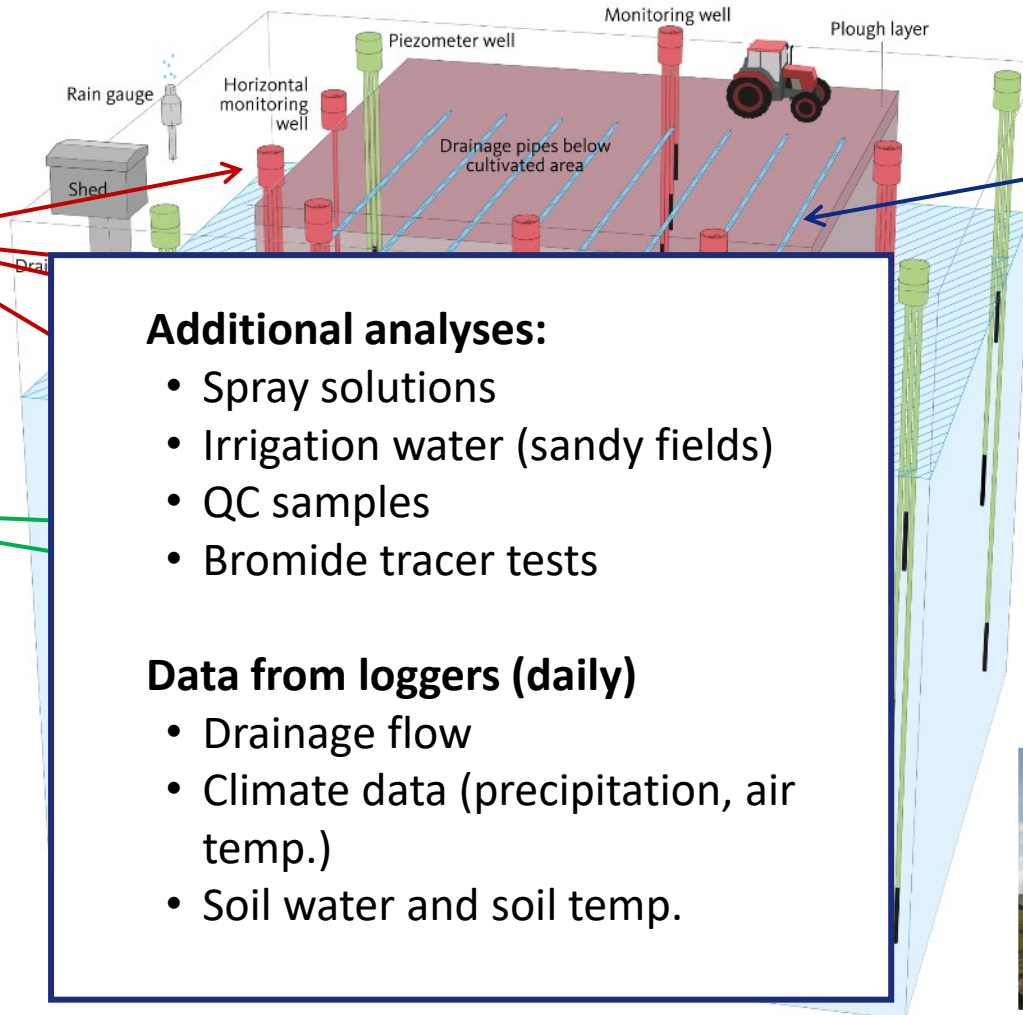
- Pesticides/TP's
- Inorganics (nitrate)

Measurement of groundwater level:

- All wells



Field size (cultivated area): 1.2-2.8 ha



Additional analyses:

- Spray solutions
- Irrigation water (sandy fields)
- QC samples
- Bromide tracer tests

Data from loggers (daily)

- Drainage flow
- Climate data (precipitation, air temp.)
- Soil water and soil temp.

Weekly:

Analysis of drainage (and groundwater – new tests):

- Pesticides/TP's
- Inorganics (pt nitrate)



PLAP tests – selection and analysis of compounds

- Selection of pesticides – Danish EPA
- Selection of pesticides and degradation products for monitoring -> EFSA conclusions
- Analyses by commercial laboratory and analytical standards from producers
- Monitoring period is 2 years (minimum)



Peer review of the pesticide risk assessment of the active substance cyazofamid

Appendix B – Used compound codes

| Code/trivial name ⁽¹⁾ | Chemical name/SMILES notation ⁽²⁾ | Structural formula ⁽³⁾ |
|----------------------------------|---|-----------------------------------|
| CCIM | 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carbonitrile <chem>Clc1nc(C#N)nc2c1ccc(C)cc2</chem> | |
| CHCN | 4-chloro-5-(4-(hydroxymethyl)phenyl)-1H-imidazole-2-carbonitrile <chem>Clc1nc(C#N)nc2c1ccc(CO)cc2</chem> | |
| CCIM-AM | 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carboxamide <chem>Clc1nc(NC(=O)C)nc2c1ccc(C)cc2</chem> | |
| CTCA | 4-chloro-5-(4-methylphenyl)-1H-imidazole-2-carboxylic acid <chem>Clc1nc(C#N)nc2c1ccc(C)cc2C(=O)O</chem> | |
| DMSA | Dimethylsulfamic acid <chem>CN(C)S(=O)(=O)O</chem> | |
| CCBA | 4-(4-chloro-2-cyano-1H-imidazol-5-yl)benzoic acid <chem>Clc1nc(C#N)nc2c1ccc(cc2)C(=O)O</chem> | |

www.efsa.europa.eu/efsajournal EFSA Journal 2016

Case study

Cyazofamid test at the
Jyndevad field
July 2020 – July 2022



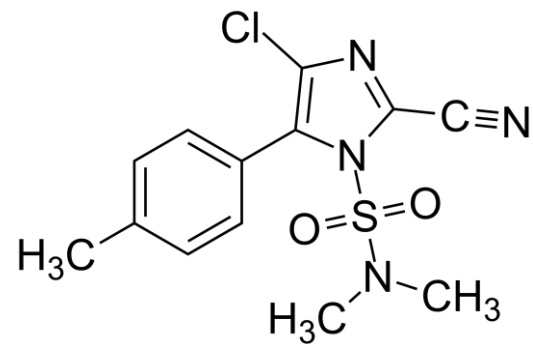
PLAP



GEUS

Background - cyazofamid

- Active ingredient - Cyazofamid
 - Fungicide
 - Downy mildew and late blight in potatoes
 - Used in Denmark since 2004



Cyazofamid



Aim of the study

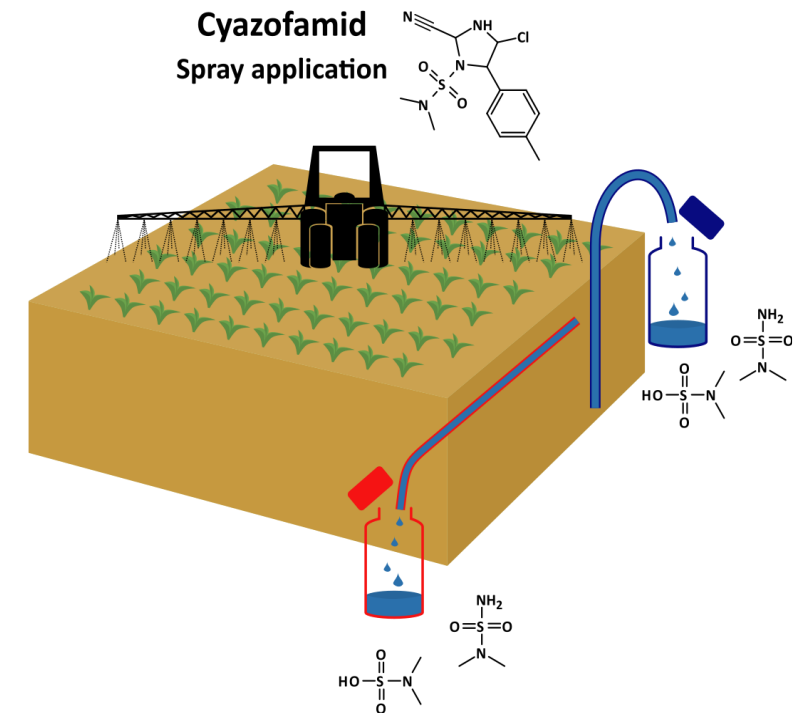
Study the potential leaching of 4 degradation products to groundwater after application of cyazofamid in a potato crop

- DMS and DMSA (not risk assessed in the EFSA conclusion)
- CTCA and CCIM (major degradation products in the EFSA conclusion)

Controlled field trial as part of the pesticide leaching programme (PLAP, www.plap.dk)

Monitoring of:

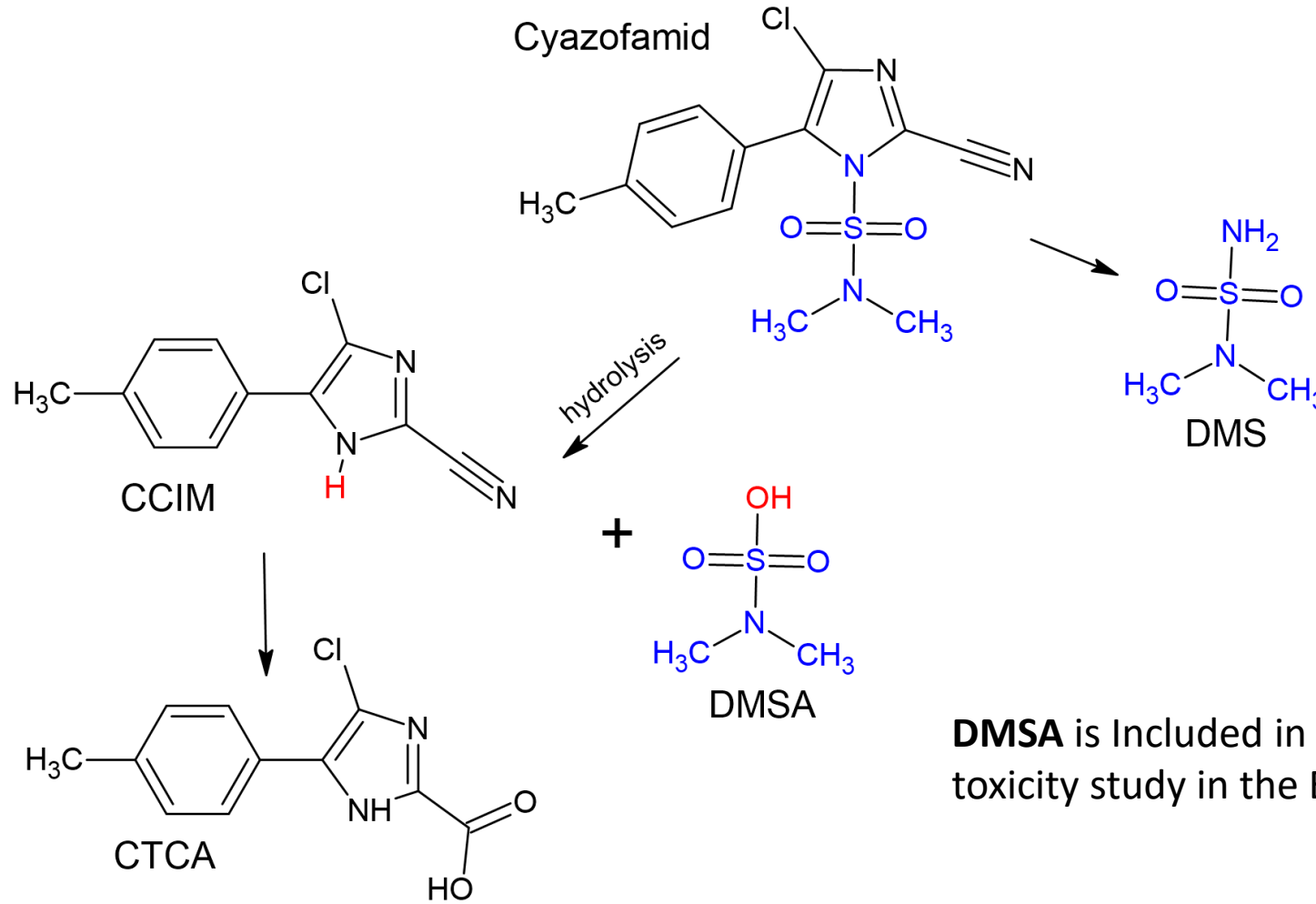
- Groundwater and soil water (suction cups, 1 mbgs)
- Spray solutions
- Irrigation water
- Climate, groundwater level etc.



Cyazofamid and degradation products – selected for monitoring



EFSA conclusion:
CCIM – major TP (31%)
CTCA – major TP (21%)

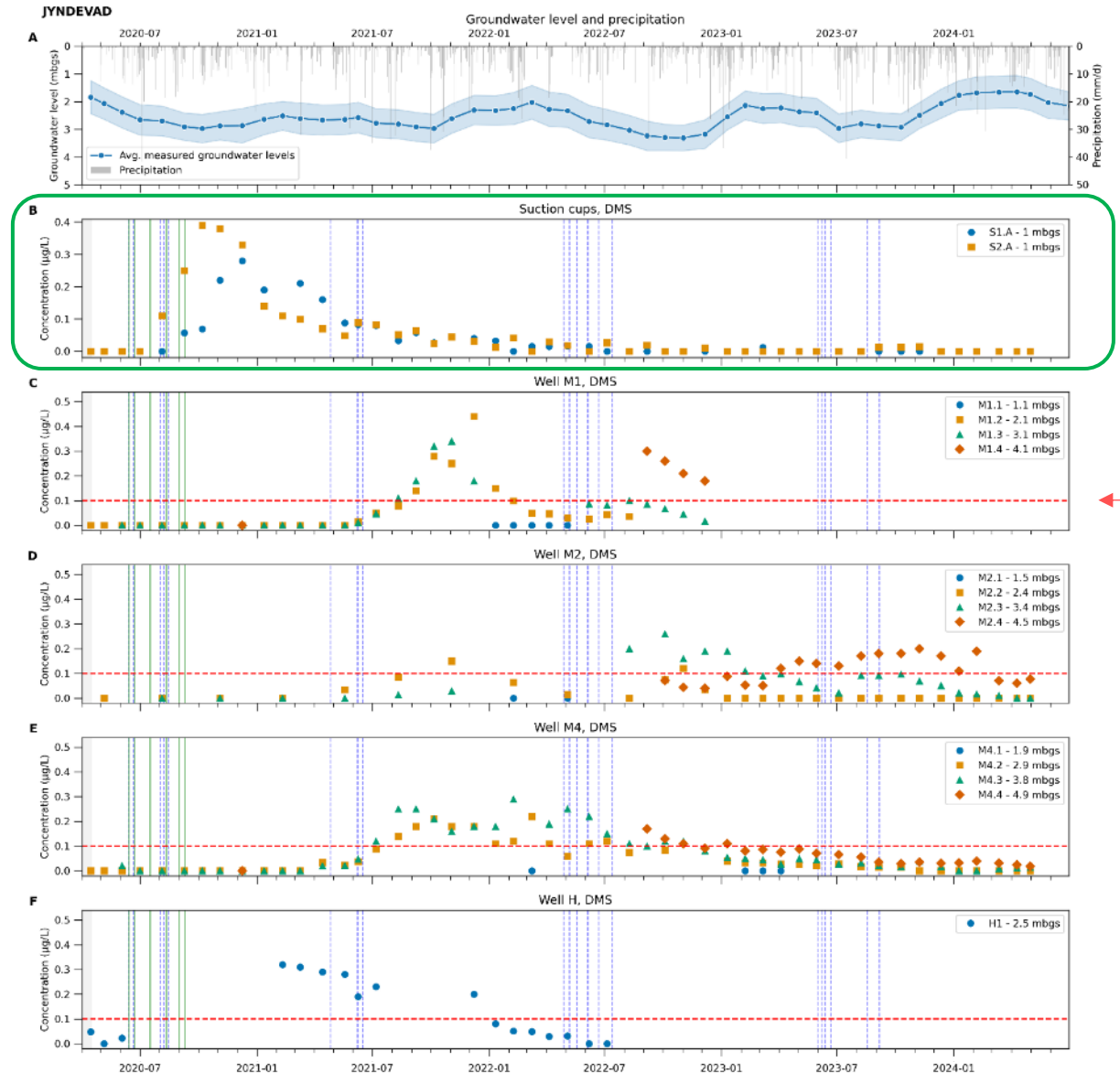
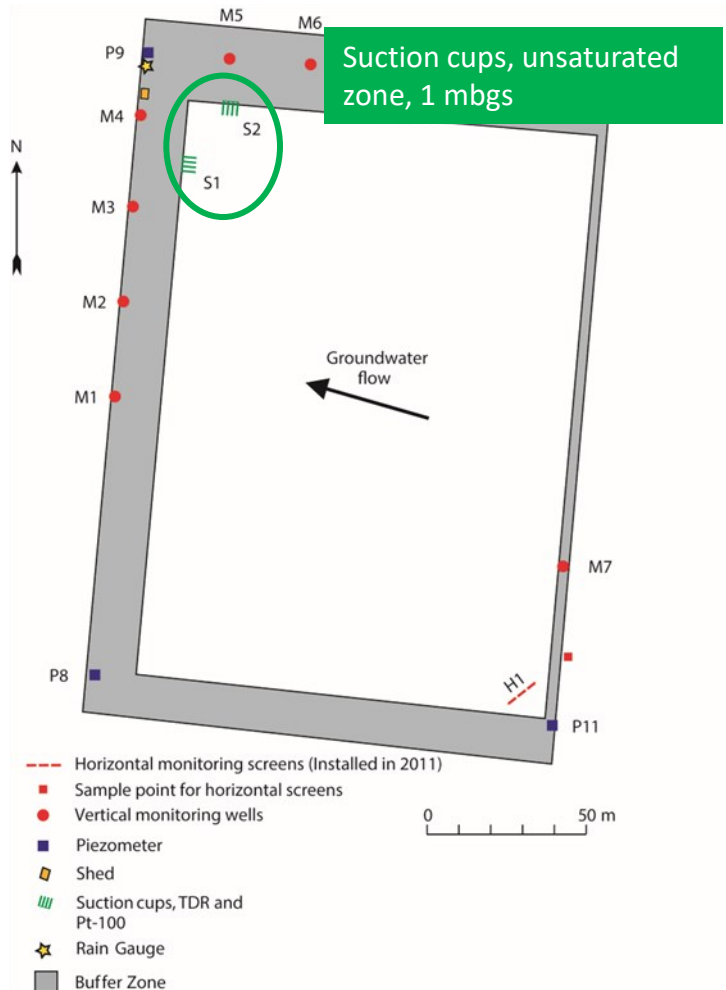


DMS is not mentioned in the EFSA conclusion
(but Previously detected at the Jyndevad field)

DMSA is Included in an acute oral toxicity study in the EFSA conclusion

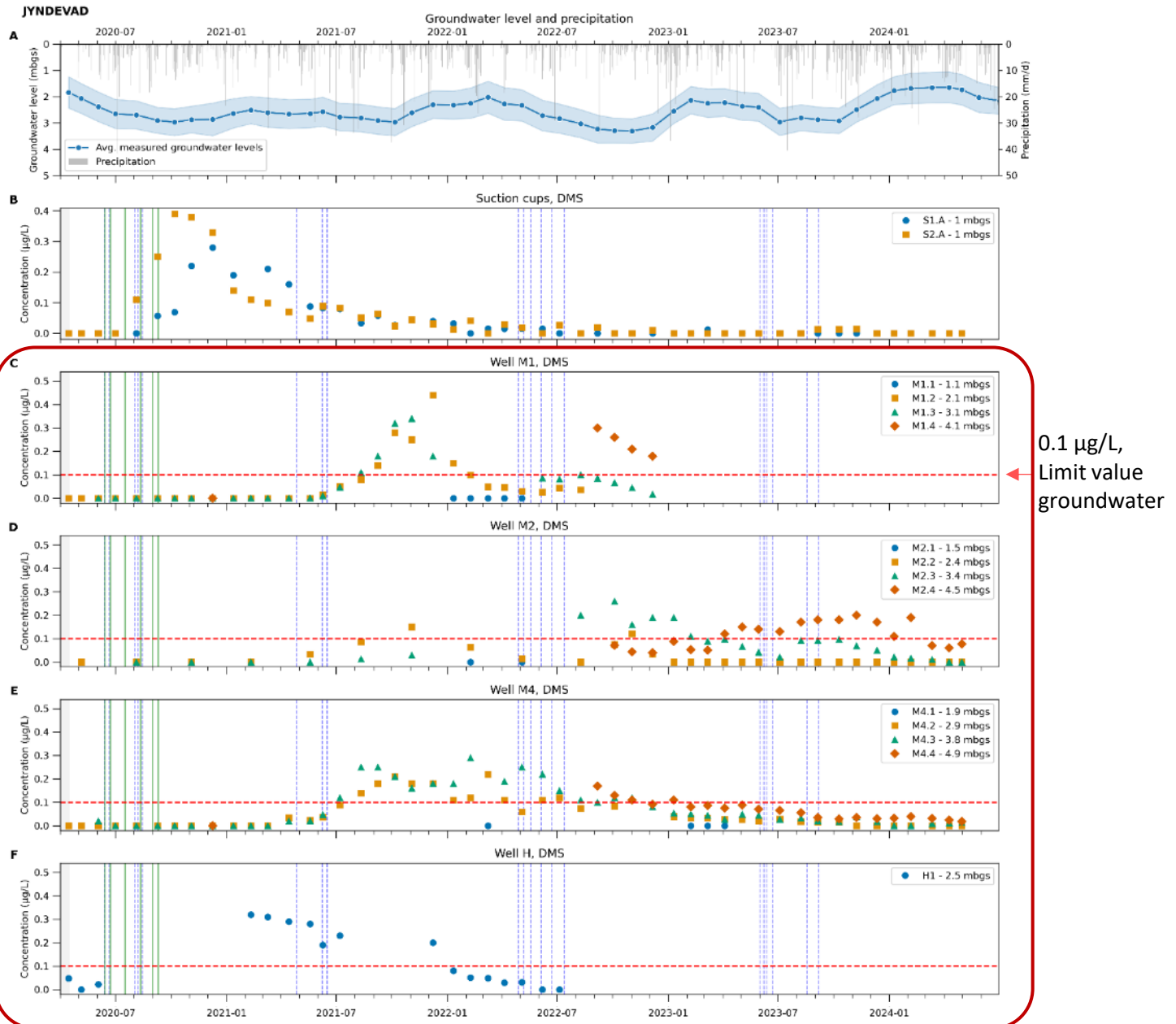
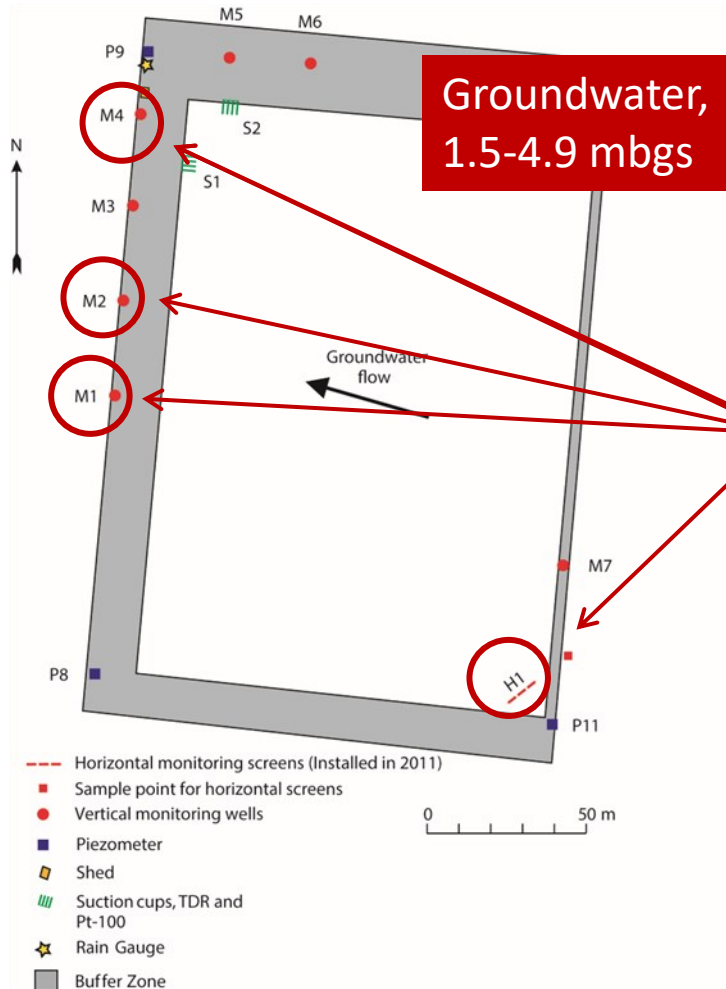
Field trial – leaching of DMS

Monitoring setup at Jyndeavad



Field trial – leaching of DMS

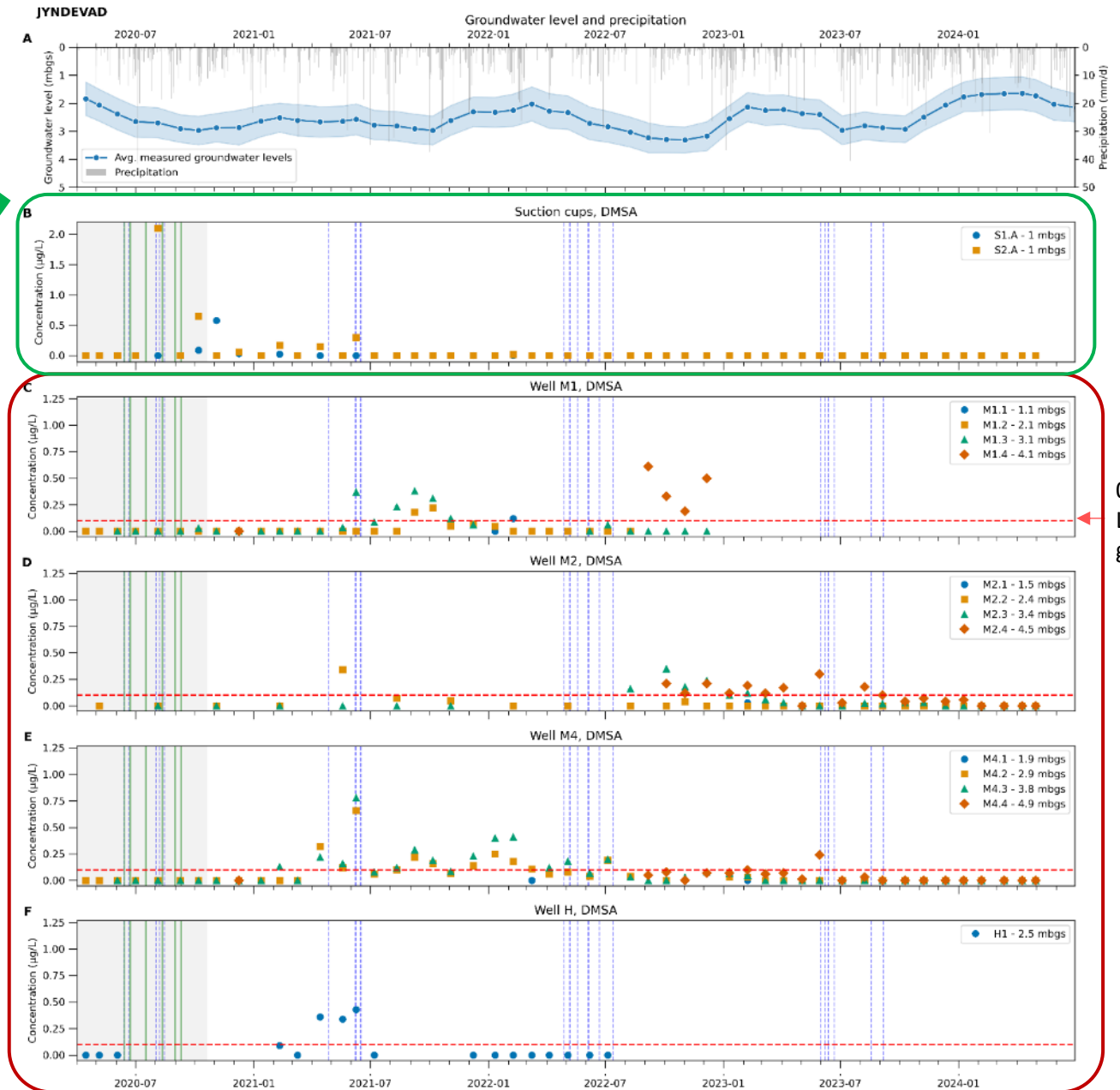
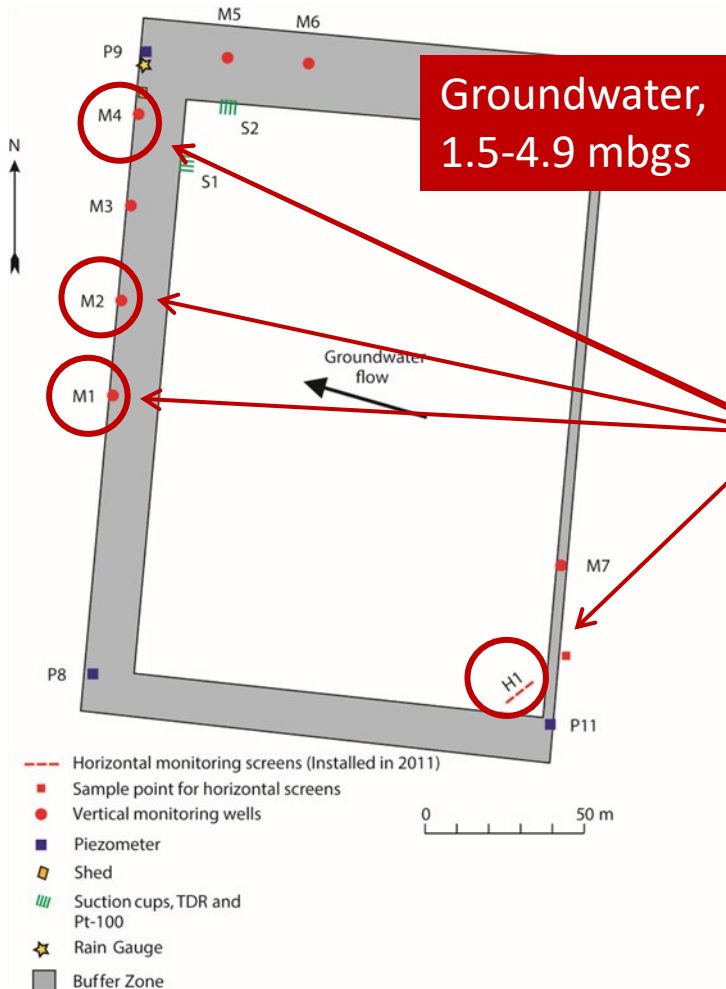
Monitoring setup at Jynde vad



Field trial – leaching of DMSA

Suction cups, unsaturated zone, 1 mbgs

Monitoring setup at Jynde vad



Conclusion on the cyazofamid test

- No detection of EFSA major metabolites CTCA and CCIM in field trial
- Leaching of DMS and DMSA, after cyazofamid application, to groundwater in concentration exceeding limit value of 0.1 µg/L.
- DMS and DMSA were not included in the risk assessment that formed the basis of EFSA's conclusion on cyazofamid => e.g. no toxicity data available...
- DMS is present in 33% of the Danish drinking water wells (> 0.1 µg/L in 7.5%)

Conclusion on the cyazofamid test

- No detection of EFSA major metabolites CTCA and CCIM in field trial
- Leaching of DMS and DMSA from field application, to groundwater exceeding limit value of 0.1 µg/L.
- DMS and DMSA were not included in the risk assessment that formed the basis of EFSA's conclusion on cyazofamid => e.g. no toxicity data available...
- DMS is present in 33% of the Danish drinking water wells (> 0.1 µg/L in 7.5%)

Danish EPA bans all cyazofamid products in Denmark from May 1, 2023

Denmark to ban groundwater polluting fungicide - after 18 years of use

Submitted by pane on January 28, 2023 - 09:57



Environmental Pollution

Volume 349, 15 May 2024, 123887



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<https://www.pan-europe.info/blog/denmark-ban-groundwater-polluting-fungicide-after-18-years-use>



Thanks for listening

More information on www.plap.dk

Nora Badawi, nba@geus.dk

