

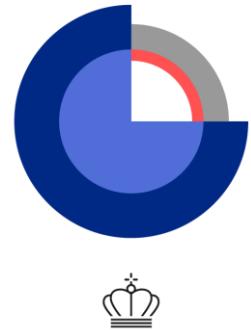
Non target screening – et stærkt værktøj til moniteringen i VAP



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www.vap-grundvand.dk (VAP)



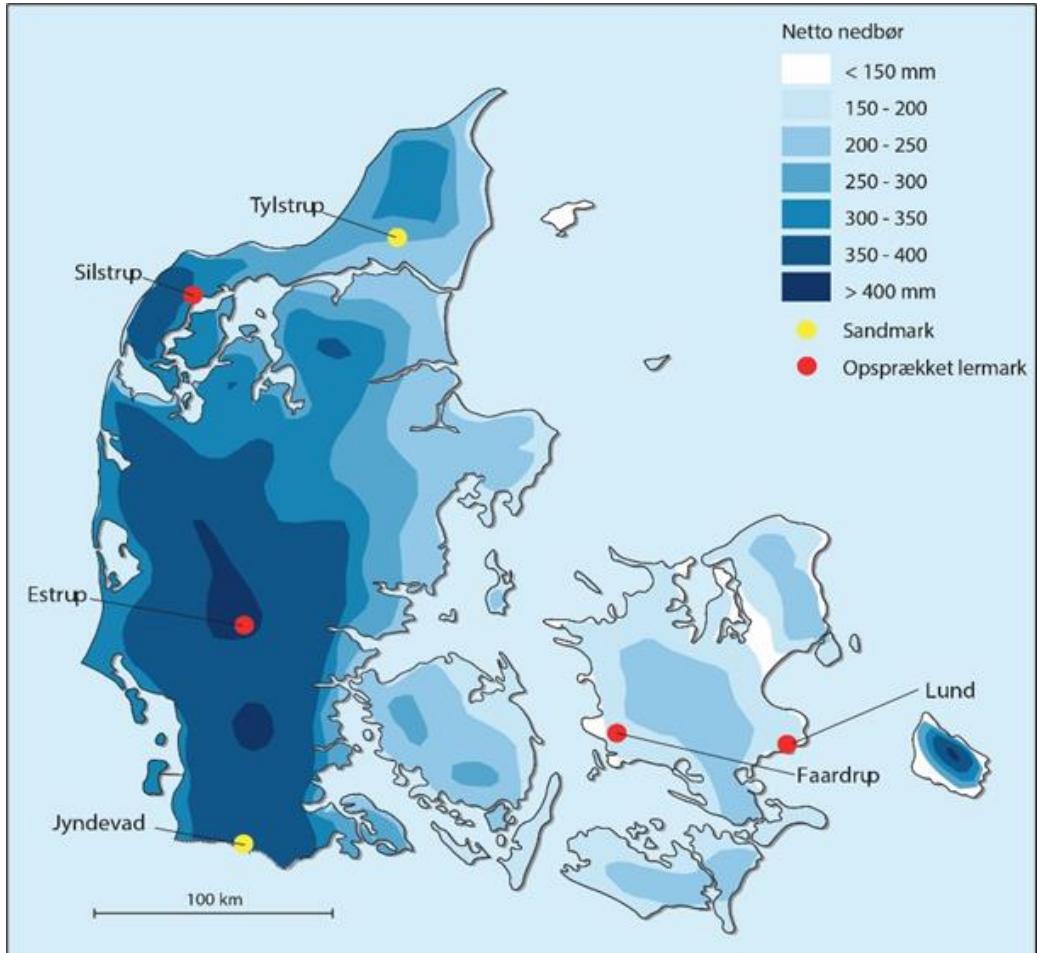
G E U S

VAP – varsligssystem for udvaskning af pesticider til grundvand

Undersøge hvorvidt regelret sprøjtning af udvalgte, godkendte pesticider på marker i omdrift kan resultere i udvaskning af pesticiderne og/eller udvalgte nedbrydningsprodukter til grundvandet i koncentrationer over de gældende kravværdier for grundvand og drikkevand

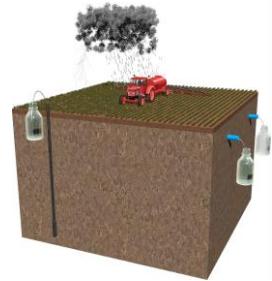
Forbedre det videnskabelige grundlag for de danske myndigheders (Miljøstyrelsen) godkendelses- og reguleringsprocedurer af pesticider

VAP – markerne



Følger god landbrugspraksis i områderne

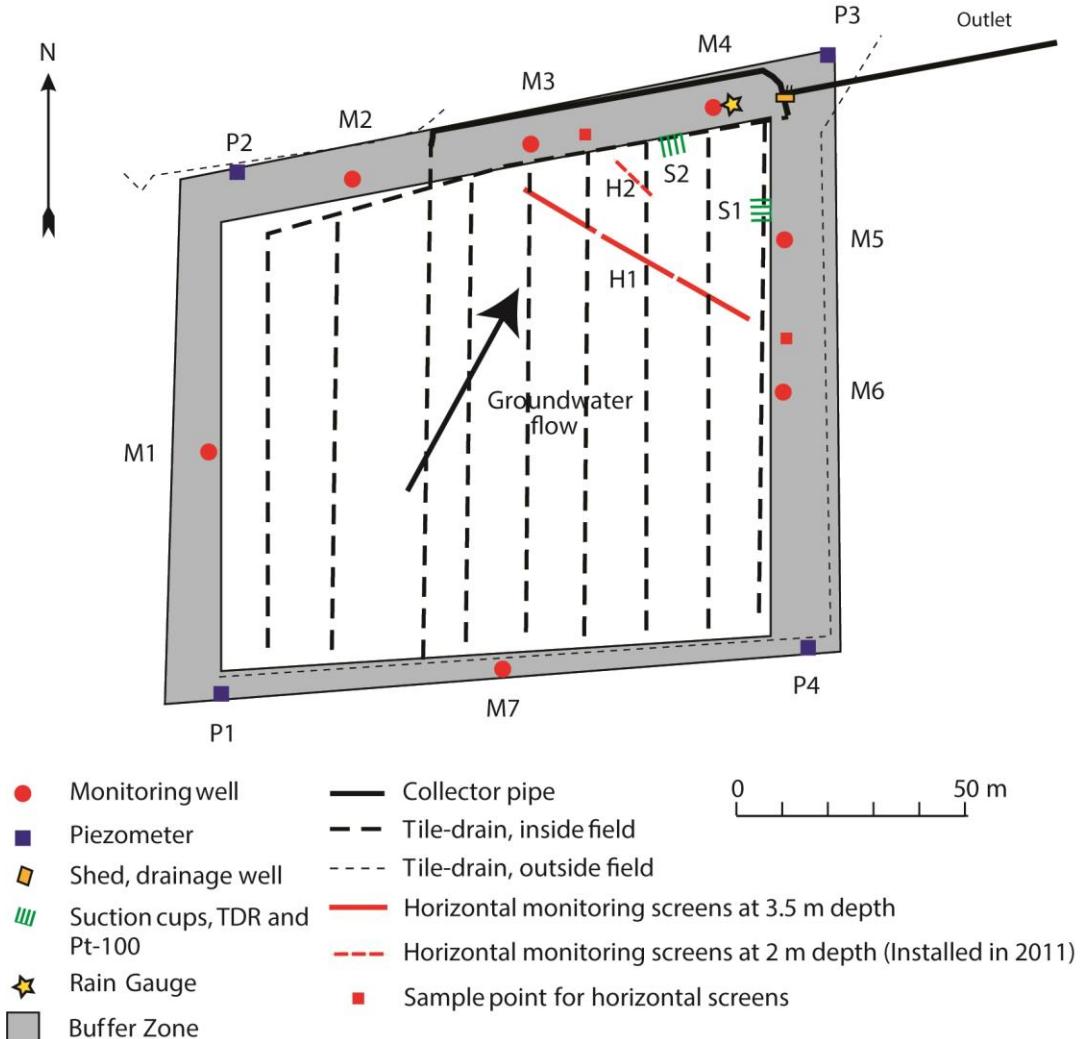
- Sædkifte
- Markbearbejdning
- Vanding
- Sprøjtning
- Høst



VAP - markinstallationer

Boringer:

- Vertikale
- Horisontale
- Sugeceller
- Pejleboringer
- Dræn



Datatyper:

- Drænvand
- Jordvand (sugeceller)
- Grundvand (1,5-5,5 mut.)
- Dybde til grundvandsspejl
- Drænflow
- Klima (nedbør, temperatur)
- Jordtemperatur
- Ledningsevne + pH
- Vandmætning

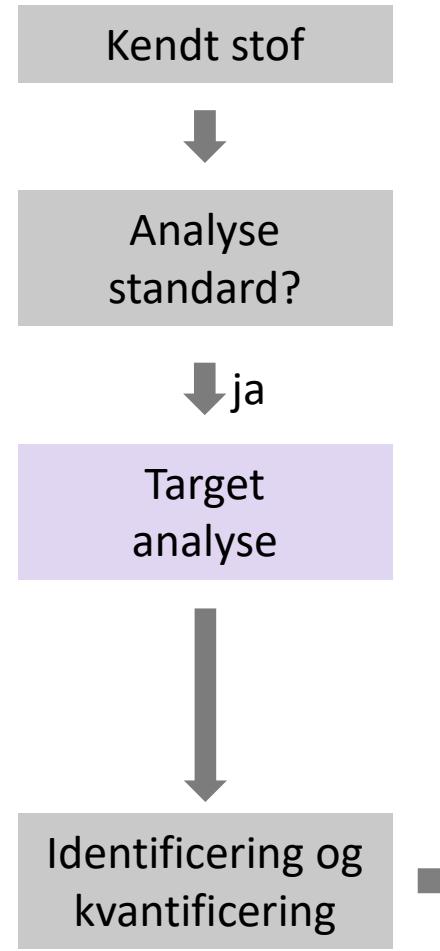
VAP - monitering

- Drænprøvetagning hver uge
- Prøvetagningsrunder hver måned
- Baggrundsprøver før sprøjtning
- Monitering i minimum 2 år
- Target analyser (LC-MSMS) for udvalgte pesticider og nedbrydningsprodukter hos kommersielt laboratorie

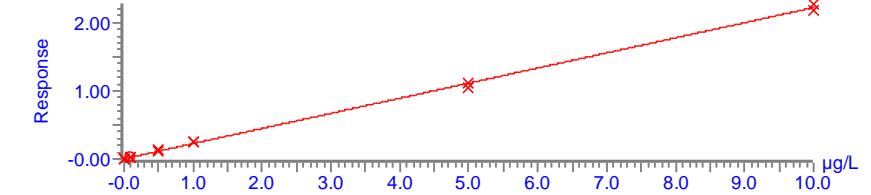


I dag: target analyse

- Baseret på en liste af udvalgte stoffer
- Forudsætning: analyse standard tilgængelig
- Vi finder kun, hvad vi leder efter



Compound name: Tebuconazole (TBZ)
Correlation coefficient: $r = 0.998654$, $r^2 = 0.997311$
Calibration curve: $0.221614 * x + 0.00352499$
Response type: Internal Std (Ref 28), Area * (IS Conc. / IS Area)
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None



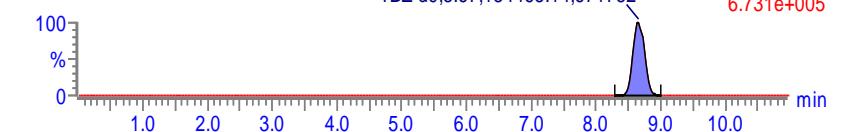
20210708_24 Smooth(Mn,3x2)
2a-9 2a-9
Tebuconazole (TBZ);8.67;395620.75;2033740
F29:MRM of 2 channels,ES+
308 > 70
2.038e+006



20210708_24 Smooth(Mn,3x2)
2a-9 2a-9
Tebuconazole (TBZ);8.67;128924.60;663497
F29:MRM of 2 channels,ES+
310 > 70
6.647e+005



20210708_24 Smooth(Mn,3x2)
2a-9 2a-9
TBZ-d9;8.67;134465.14;671782
F31:MRM of 2 channels,ES+
317 > 70
6.731e+005



I dag: udvælgelse af produkter og analytter



European Food Safety Authority

EFSA Journal 2014;12(1):3485

CONCLUSION ON PESTICIDE PEER REVIEW

Conclusion on the peer review of the pesticide risk assessment of the active substance tebuconazole¹

European Food Safety Authority²
European Food Safety Authority (EFSA), Parma, Italy

ABSTRACT
The conclusion on the peer review of the pesticide risk assessment of the active substance tebuconazole¹ is based on the available scientific information on the properties, uses and exposure data for the active substance, its metabolites and impurities, and the results of the risk assessment. The conclusion is valid for the uses and conditions of use described in the application and for the geographical area covered by the application. The conclusion is also valid for other uses and conditions of use if they are consistent with the properties and exposure data used in the risk assessment. The conclusion is also valid for other geographical areas if they are consistent with the properties and exposure data used in the risk assessment.

KEY WORDS
tebuconazole, p

APPENDIX B – USED COMPOUND CODE(S)

Code/Trivial name*	Chemical name**	Structural formula***
1,2,4-triazole	1H-1,2,4-triazole	
HWG 1608-lactone M17	5-tert-butyl-5-(1H-1,2,4-triazol-1-ylmethyl)dihydrofuran-2(3H)-one	
HWG 1608-pentanoic acid M25	4-hydroxy-5,5-dimethyl-4-(1H-1,2,4-triazol-1-ylmethyl)hexanoic acid	
hydroxy-tebuconazole M03	5-(4-chlorophenyl)-2,2-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)pentane-1,3-diol	

Godkendte produkter (aktivstof):

- Godkendt for første gang i DK eller er fornyet ved vurdering i EU
- Allerede testede stoffer (understøttende test til regulering i MST)
- Opfølgning fra massescreeninger, EU viden etc.

Udvælgelse af stoffer til monitering:

- EFSA conclusions:
 - Nævnt som *major metabolites* i miljøet
 - Udvasker i modelleringen > 0,1 µg/L
 - Ny viden fra EFSA, litteraturen, nabolandene etc...

Test af tebuconazole i VAP

 European Food Safety Authority

EFSA Journal 2014;12(1):3485

CONCLUSION ON PESTICIDE PEER REVIEW

Conclusion on the peer review of the pesticide risk assessment of the active substance tebuconazole¹

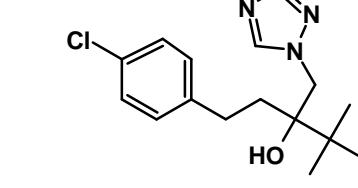
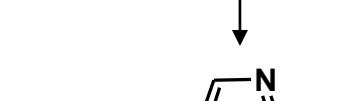
European Food Safety Authority²
European Food Safety Authority (EFSA), Parma, Italy

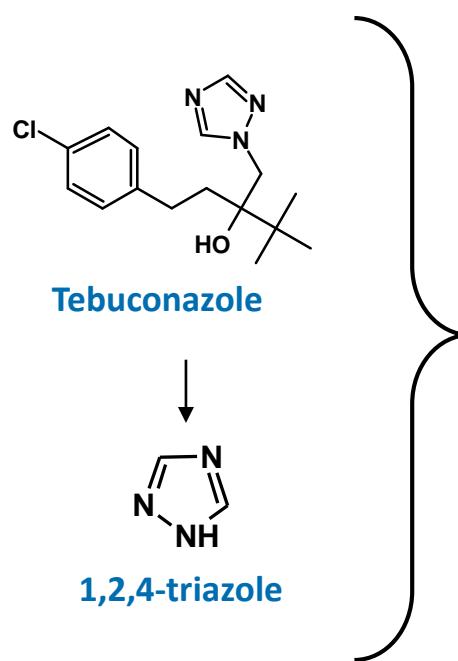
ABSTRACT
The conclusion assessments can active substance No 1107/2009, tebuconazole as regulator in oil assessment, der information idea

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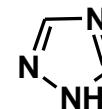
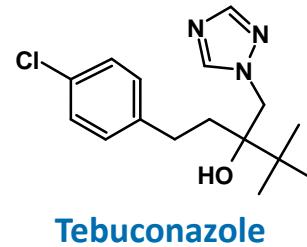
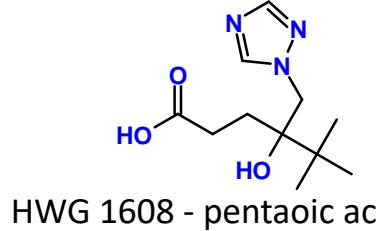
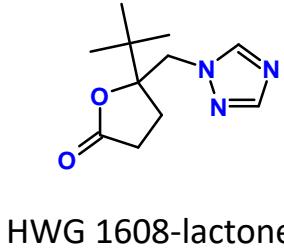
Jord- og grundvandsmetab. (EFSA)

Aerob nedbrydning i jord →
Tebuconazole og 1,2,4-triazole
Inkluderet i moniteringen

EFSA Journal 2014;12(1):3485, tebuconazole

Tebuconazole – kendte metabolitter (EFSA, litt.)

Fotolyse lab. (EFSA)

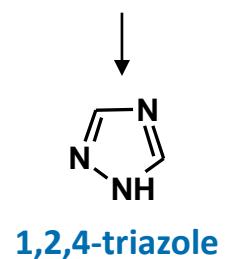
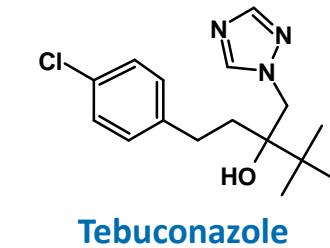
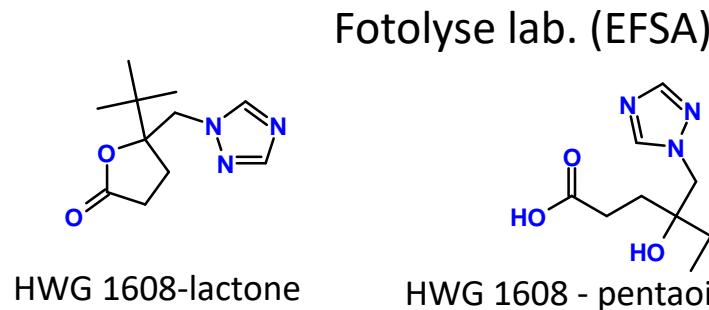


1,2,4-triazole

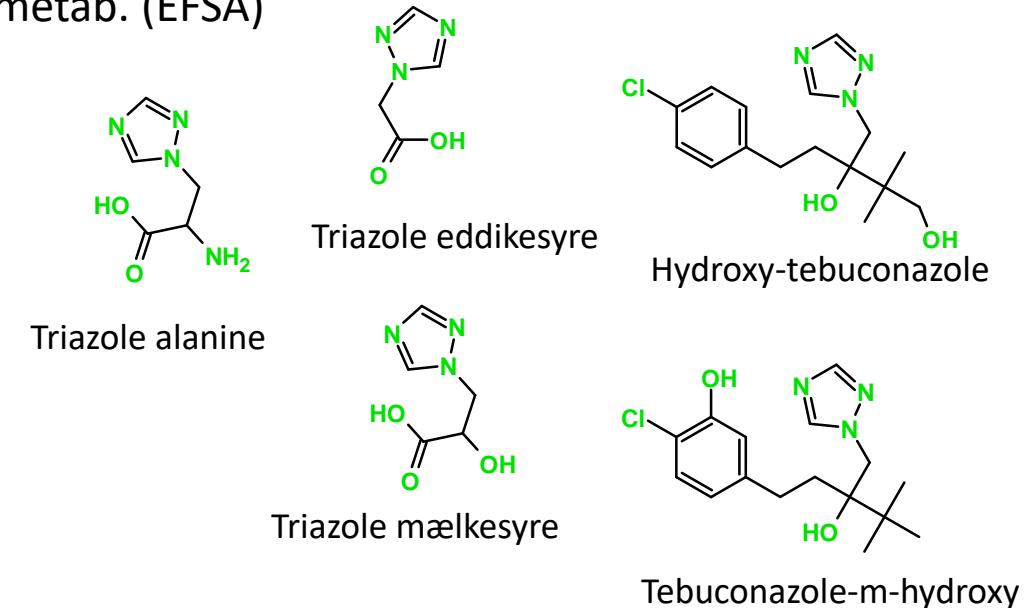
Jord- og grundvandsmetab. (EFSA)

EFSA Journal 2014;12(1):3485, tebuconazole

Tebuconazole – kendte metabolitter (EFSA, litt.)



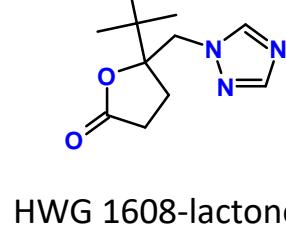
Plantemetab. (EFSA)



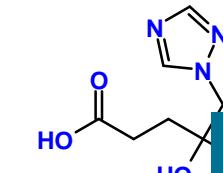
Jord- og grundvandsmetab. (EFSA)

EFSA Journal 2014;12(1):3485, tebuconazole

Tebuconazole – kendte metabolitter (EFSA, litt.)

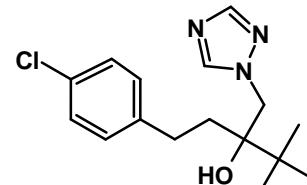


Fotolyse lab. (EFSA)

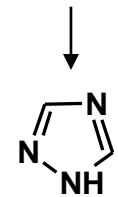


HWG 1608 - pentaioic acid

EFSA -10 metabolitter

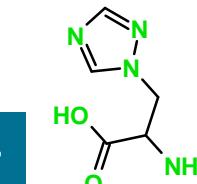


Tebuconazole

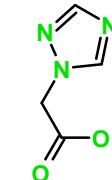


1,2,4-triazole

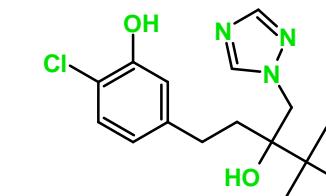
Plantemetab. (EFSA)



Triazole eddikesyre



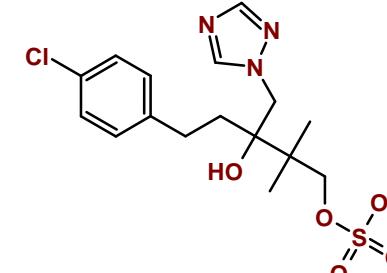
The chemical structure of Hydroxy-tebuconazole is shown. It consists of a 4-chlorophenyl ring connected via a methylene group to a central carbon atom. This central carbon is also bonded to a 1-methylimidazole ring, a hydroxymethyl group (-CH₂OH), and a tert-butyl group. The hydroxymethyl group and the tert-butyl group both have green 'HO' labels above them, indicating they are chiral centers.



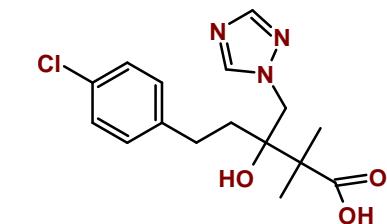
Tebuconazole-m-hydroxy



Triazole mælkesyre



hydroxy-tebuconazole-sulfate



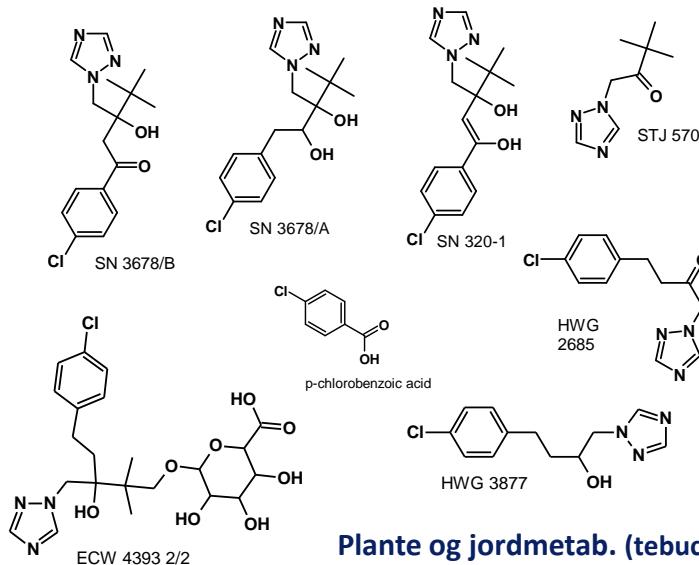
Tebuconazole-carboxylic acid

Jord- og grundvandsmetab. (EFSA)

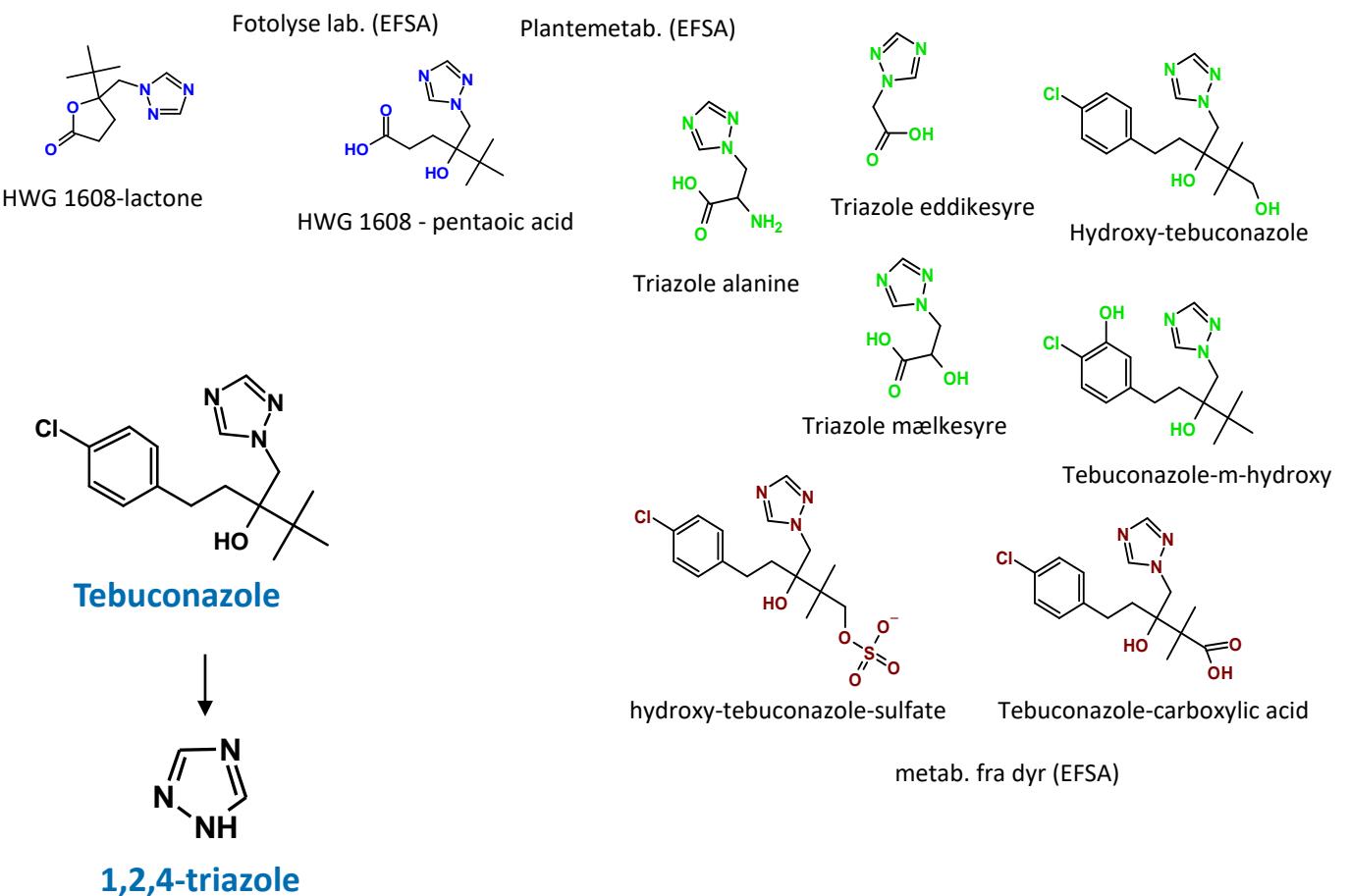
metab. fra dyr (EFSA)

EFSA Journal 2014;12(1):3485, tebuconazole

Tebuconazole – kendte metabolitter fra suspect screening



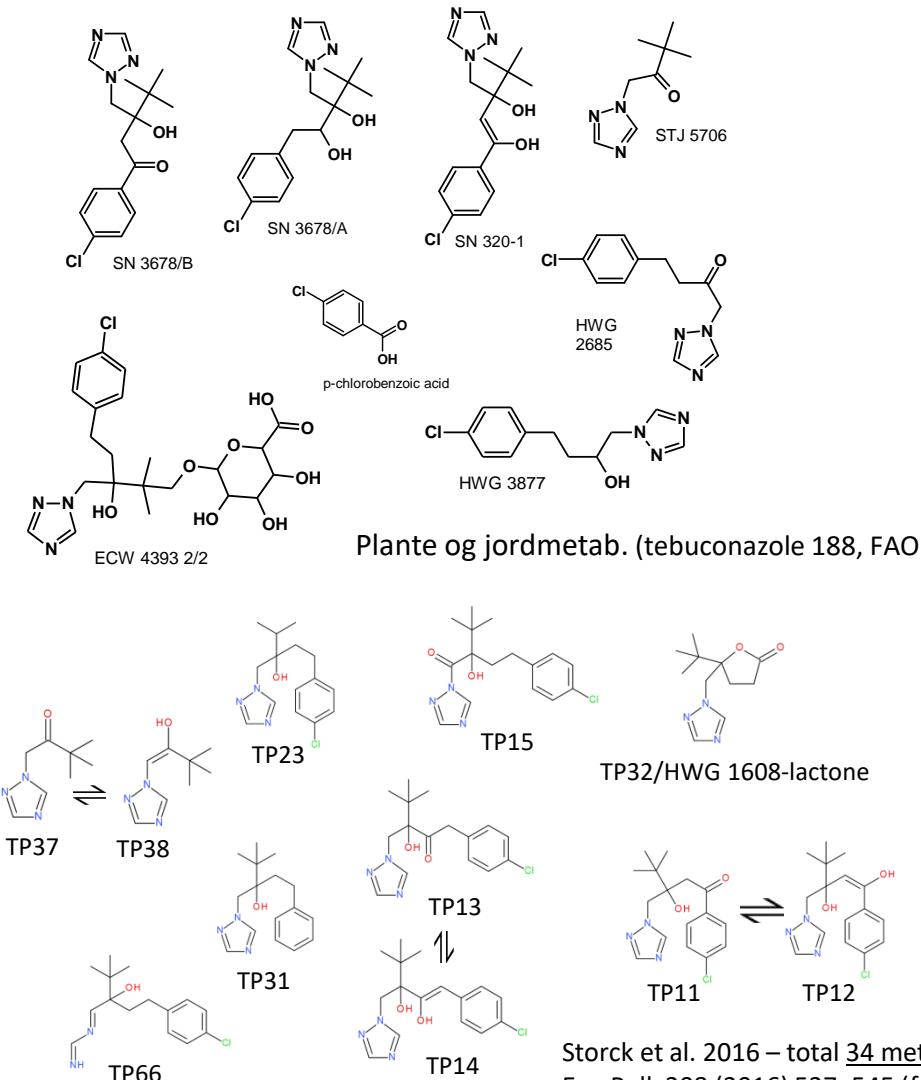
Plante og jordmetab. (tebuconazole 188, FAO)



Jord- og grundvandsmetab. (EFSA)

EFSA Journal 2014;12(1):3485, tebuconazole

Tebuconazole – kendte metabolitter fra suspect screening



> 50 tebuconazole metabolitter i litteraturen

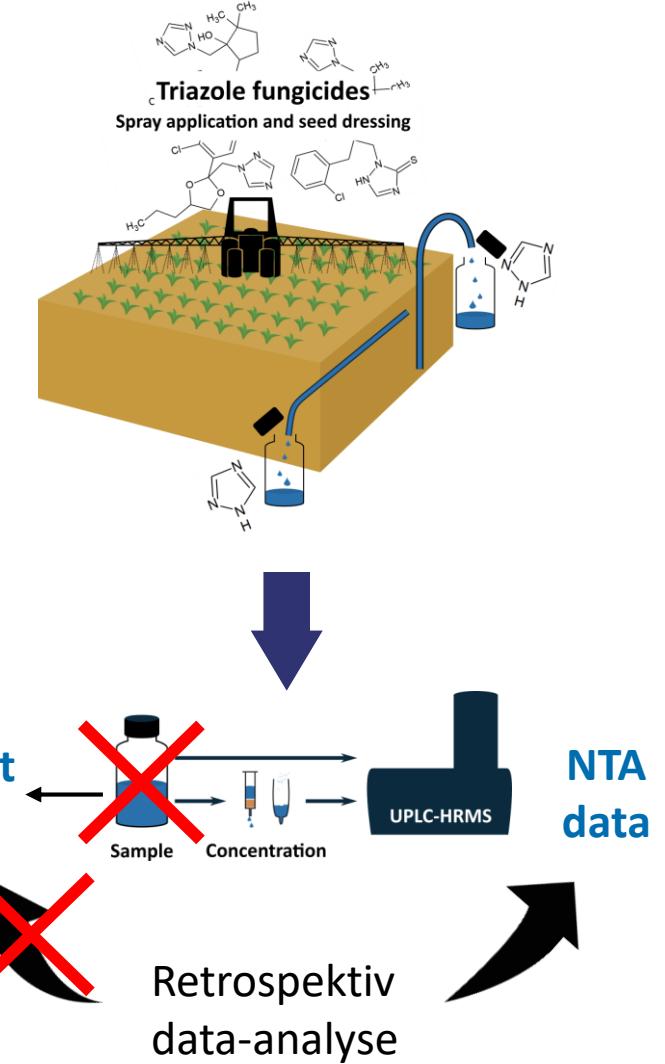
NTA til monitering i VAP

Fordele:

- NTA af vandprøver løbende efter sprøjtning
 - Mulighed for at screene for flere metabolitter end med taget-analyse
 - Suspect screening for alle metabolitter fra pesticid (iht EFSA conclusion, FAO etc)
 - Verificere suspects med analyse-standard
- Fokuseret taget-analyse ved ekstra test af aktivstof
- NTA af baggrundsprøver
 - Mulighed for at kigge efter suspects før sprøjtning med aktivstof
- Retrospektiv analyse af alle prøver
- Støttestudier til VAP monitering:
 - Nedbrydningsstudier i jord til identification af nedbrydningsprodukter (suspect og non-target screening)

Ulemper/udfordringer:

- Opsætning af standardmetode til grundvandsrelevante stoffer
- Tidskrævende (og deraf relativt dyrt)
- Forskningsbaseret

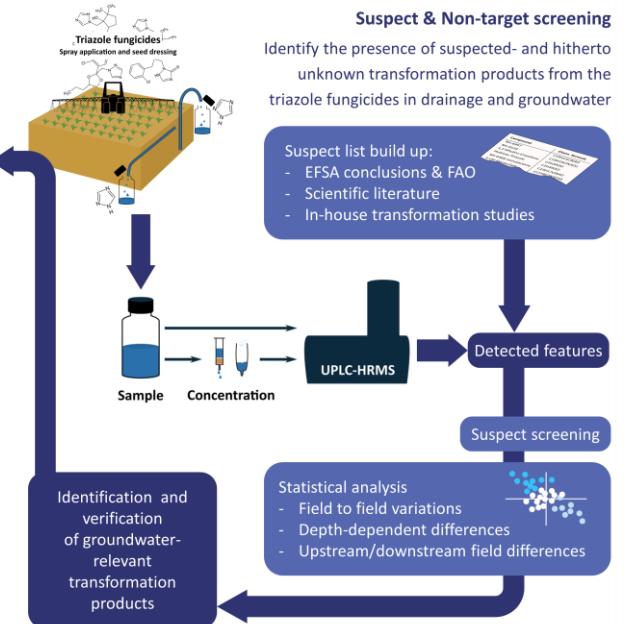
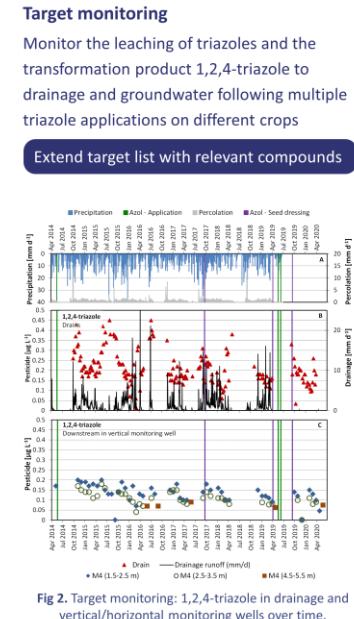


Status på NTA i VAP – forskning

Jord- og vandprøver fra VAP

- Suspectliste med 52 tebuconazole metabolitter
- Suspectliste med 193 azol metabolitter fra litteraturen (Anvendt 9 forskellige azoler på VAP-markene siden 1999)
- Suspect screening for alle kendte metabolitter fra alle anvendte pesticider (75 aktivstoffer) i VAP
 - påbegyndt suspect-liste

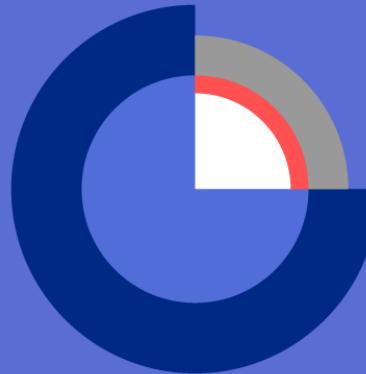
Compound	Chem. formula
RH-6467	C19H15ClN4O
RH-229	C19H16ClN3O2
1,2-dihydro-triazole	C2H3N3O
Hydroxy-triazole	C2H3NAO
RH-6468 iminolactone	C19H17ClN4O
5-OH Florasulam	C11H6E3N3O2S





Tak for opmærksomheden

www.vap-grundvand.dk



G E U S