Removing pesticides from greenhouse effluent water

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Problem definition

- Agricultural use of pesticides has a major impact on surface water
- Besides a reduction in the use of pesticides, also end-of-pipe solution could be used to improve quality of surface water
- For instance, the use of filter techniques
- Efficiency of these techniques under practical condition not well understood

Objective

- Evaluate techniques for removing pesticides from greenhouse effluent in a standardised and reproducible way

Materials and methods

- Standard water
  - Pesticides
  - Macro & micro nutrients
- Pesticide removal techniques
  - Activated carbon
  - UV / peroxide
  - Filtration
  - Biological

Standard water: Selection of pesticides

- Expert study
- Selection criteria
  - relevant for EU Water Framework Directive
  - present in greenhouse effluent water
  - registered for use in greenhouse horticulture in NL
  - detectable with conventional analytical techniques

Standard water: nutrients

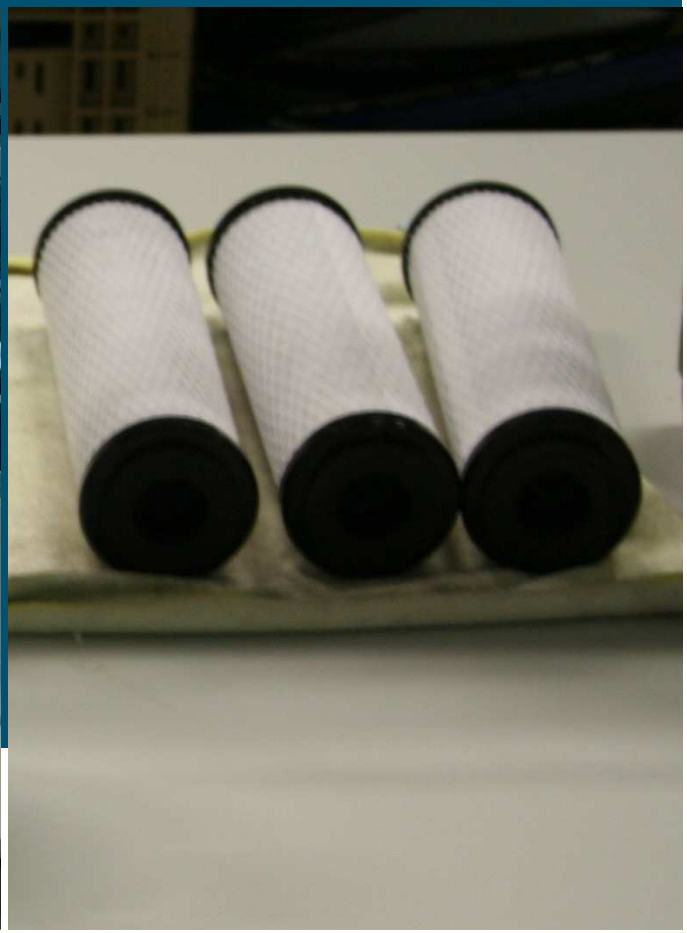
- Selection criteria
  - Common practice
  - Mix of recipes for cut-flowers and fruit vegetables
  - Maximum values

Methods and materials

- Activated carbon set-up
  - Targeted amount = 7000 L
  - Targeted sampling scheme = 0, 10, 25, 50, 100, 200, 300, 400 h

Methods and materials

- Activated carbon
  - Flow setting = 20 L h^{-1}
  - Volume activated coal: 0.62 L



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Methods and materials

- Liquid chromatography – mass spectrometry
- Method development

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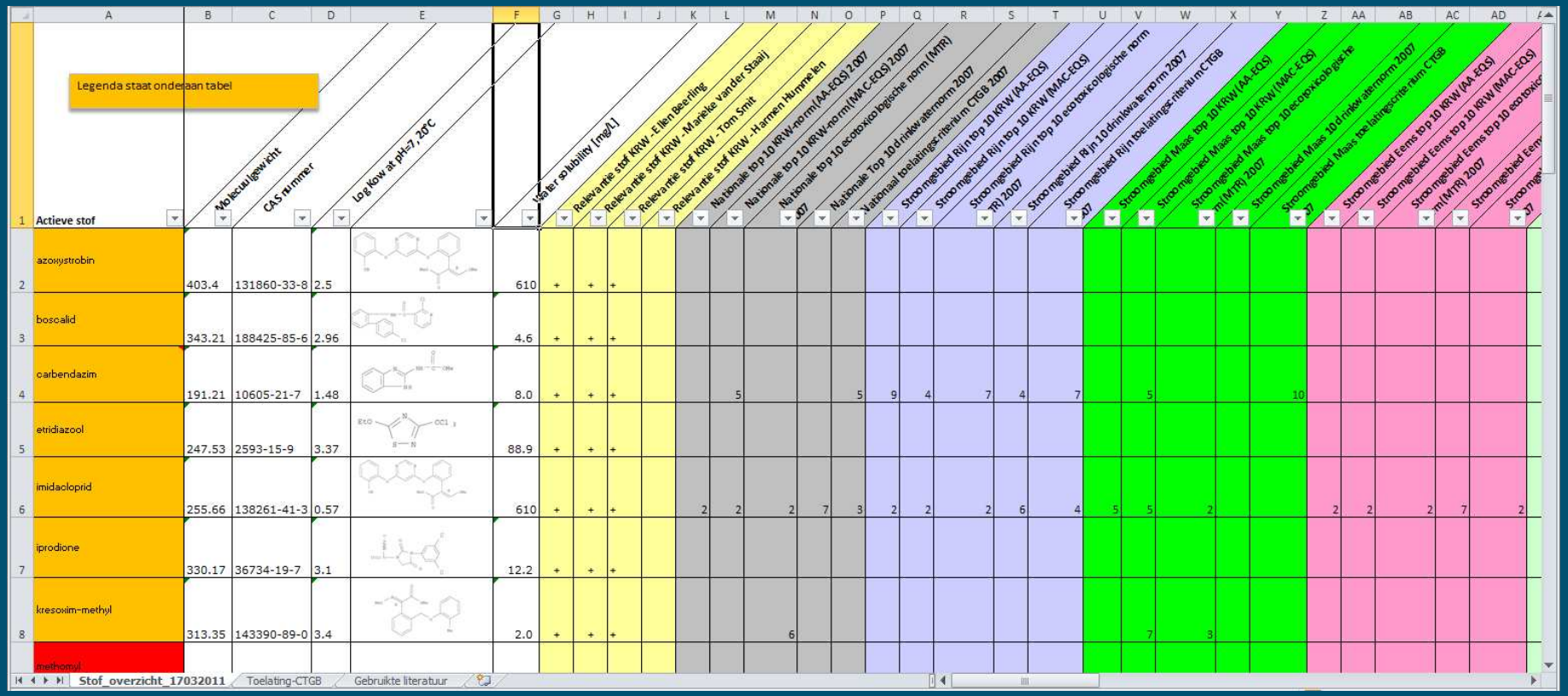
Results: selection of active ingredients



Actieve stof	Molecuulgewicht	CAS nummer	Log Kow at pH=7, 20°C	Water solubility [mg/L]	Relevante stof KRW - Ellen Beerling	Relevante stof KRW - Marieke vander Staaij	Relevante stof KRW - Tom Smit	Relevante stof KRW - Harmen Hummelen	Nationale top 10 KRW-norm (AA-EQS) 2007	Nationale top 10 KRW-norm (MAC-EQS) 2007	Nationale top 10 ecotoxicologische norm (MTR)	Nationale Top 10 drinkwaternorm 2007	Nationaal toelatingscriterium CTGB 2007	Stroomgebied Rijn top 10 KRW (AA-EQS)	Stroomgebied Rijn top 10 KRW (MAC-EQS)	Stroomgebied Rijn top 10 ecotoxicologische norm (MTR) 2007	Stroomgebied Rijn 10 drinkwaternorm 2007	Stroomgebied Rijn toelatingscriterium CTGB	Stroomgebied Maas top 10 KRW (AA-EQS)	Stroomgebied Maas top 10 KRW (MAC-EQS)	Stroomgebied Maas top 10 ecotoxicologische norm (MTR) 2007	Stroomgebied Maas 10 drinkwaternorm 2007	Stroomgebied Maas toelatingscriterium CTGB	Stroomgebied Eems top 10 KRW (AA-EQS)	Stroomgebied Eems top 10 KRW (MAC-EQS)	Stroomgebied Eems top 10 ecotoxicologische norm (MTR) 2007
azoxystrobin	403.4	131860-33-8	2.5	610	+	+	+																			
boscalid	343.21	188425-85-6	2.96	4.6	+	+	+																			
carbendazim	191.21	10605-21-7	1.48	8.0	+	+	+			5			5	9	4	7	4	7		5		10					
etridiazool	247.53	2593-15-9	3.37	88.9	+	+	+																			
imidacloprid	255.66	138261-41-3	0.57	610	+	+	+		2	2	2	7	3	2	2	2	6	4	5	5	2		2	2	2	7	2
iprodione	330.17	36734-19-7	3.1	12.2	+	+	+																			
kresoxim-methyl	313.35	143390-89-0	3.4	2.0	+	+	+				6									7	3					
methomyl																										

Legenda staat onderaan tabel

Stof_overzicht_17032011 | Toelating-CTGB | Gebruikte literatuur

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Results: selection of products

Product	Type	Active ingredient	Formulation [gr L^{-1}]	Target concentration [µg L^{-1}]
ORTIVA	Liquid	azoxystrobin	250	1
COLLIS	Liquid	boscalid kresoxim-methyl	boscalid: 200 kresoxim methyl: 100	1
TOPSIN	Liquid	carbendazim (breakdown product of thiofanaat-methyl)	500	1
AATERRA ME	Liquid	etridiazool	700	1
ADMIRE	Korrel	imidacloprid	70% imidacloprid	1
ROVRAL AQUAFLO	Liquid	iprodione	500	1
RUNNER	Liquid	methoxyfenozide	240	1
PIRIMOR	Granule	pirimicarb	50% pirimicarb	1
PLENUM 50 WG	Granule	pymetrozine	50% pymetrozine	1
CALYPSO	Liquid	thiacloprid	480	1
RIZOLEX	Liquid	tolclofos-methyl	500	1

Results: selection of nutrients

- Macro nutrients

Macro nutrients	Concentration [mmol L^{-1}]
NH_4	0.5
K	7.0
Na	6.0
Ca	8.0
Mg	3.5
NO_3	17.0
Cl	6.0
SO_4	6.0
HCO_3	1.0
P (H_2PO_4)	0.7

Results: selection of nutrients

- Micro nutrients

Micro nutrients	Concentration [µmol L^{-1}]
Fe	50
Mn	20
Zn	5
B	50
Cu	2
Mb	1

Results: method development

- Limit of quantification (LOQ)

Active ingredient	LOQ [ppt]
azoxystrobin	5
boscalid	40
kresoxim-methyl	40
carbendazim (breakdown product of thiofanaat-methyl)	20
etridiazool	n.d.
imidacloprid	40
iprodione	20
methoxyfenozide	20
pirimicarb	20
pymetrozine	0.1
thiacloprid	20
tolclofos-methyl	20

Results: selection of fertiliser

Substance	Concentration [L m^{-3}]
Potassium nitric acid	0.086
Potassium sulphuric acid	1.321
Potassium phosphorus carbonate	0.255
Potassium carbonate	0.472
Calcium nitrate	1.628
Magnasium nitrate	0.383
Ammonium nitrate	0.050
Iron chelate DTPA 6%	1.125
Borax	1.800
Copper sulphate	1.000
Natrium molybdate	0.500
Zink sulphate	0.800
Manganese sulphate	2.000

Remarks

- Start concentration of a.i. too high
- Variation in flow
  - Noticed flow: 5-20 L h^{-1}
  - Pollution of activated carbon
  - Risk of not-well mixed influent
  - Risk of photolytic breakdown

Recommendations

- Recommendations:
  - Measure the flow through activated carbon continuously
  - Consider mixing of incoming flow
  - Add pre-filter to remove pollutant
  - Cover tanks to prevent photolytic breakdown
  - Consider the addition of well defined organic pollutants and adjuvants

What's next?

- Continuing activated carbon experiments
- Testing other pesticide removal principles
  - UV / peroxide
  - Filtration
  - Biological

Acknowledgement

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