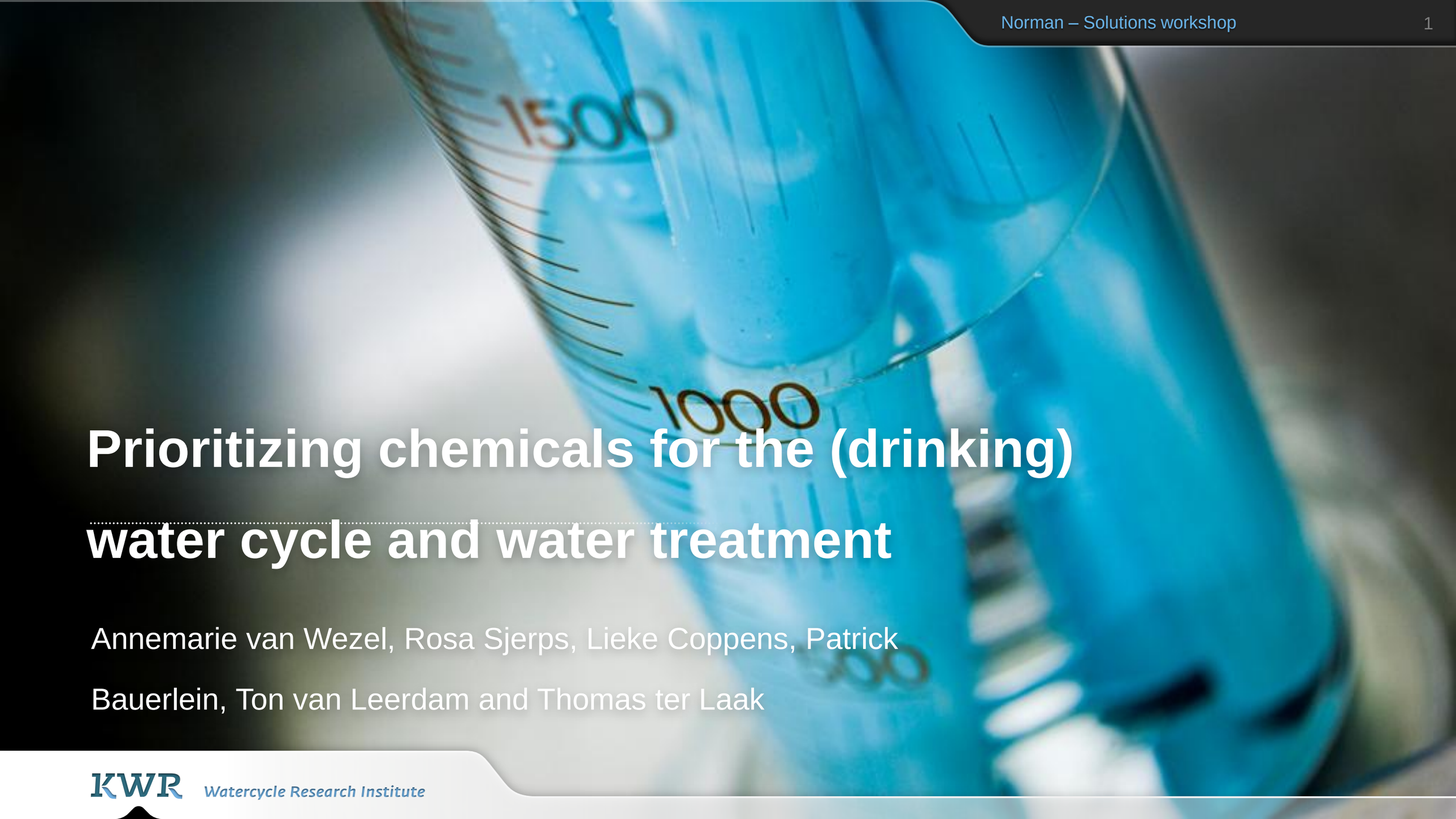
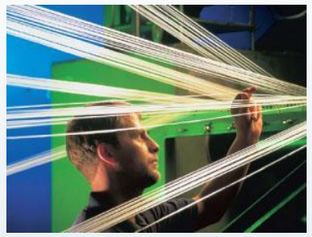


Prioritizing chemicals for the (drinking) water cycle and water treatment

Annemarie van Wezel, Rosa Sjerps, Lieke Coppens, Patrick Bauerlein, Ton van Leerdam and Thomas ter Laak

KWR Watercycle Research Institute

Chemicals; we use them all for benificial purposes



Crop Protection

Pharmaceutic

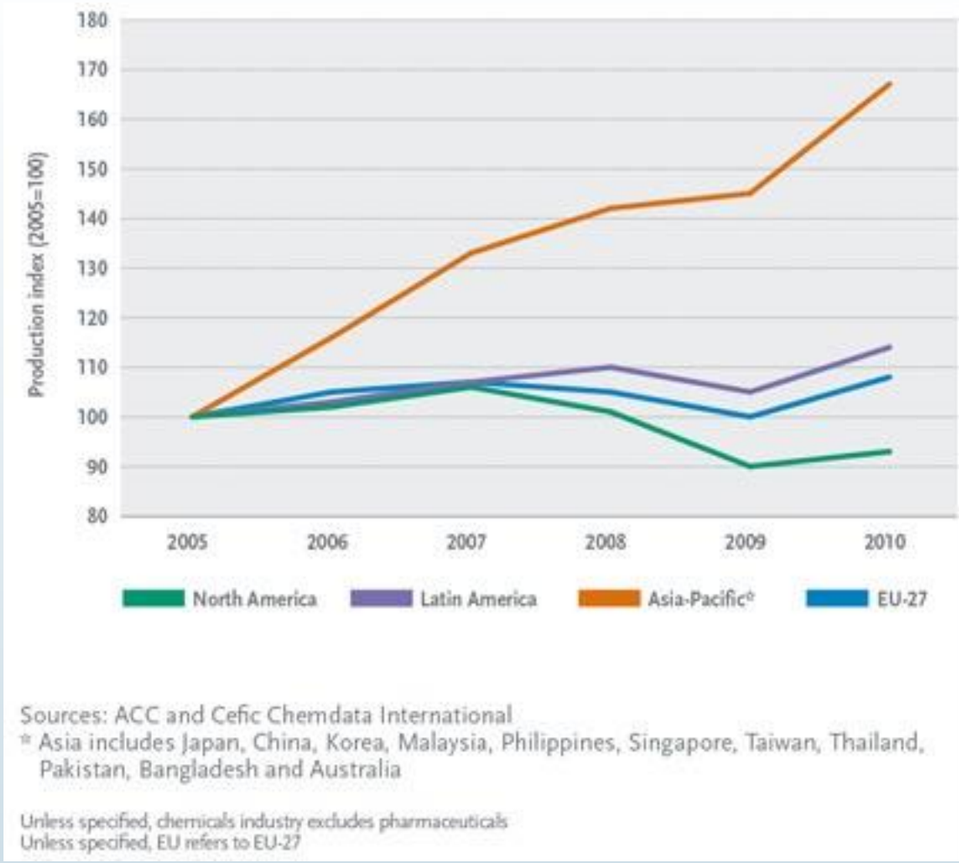
Food Supplements

Artificial Fibers

Cosmetics

Paints & Coatings

Flame Retardants

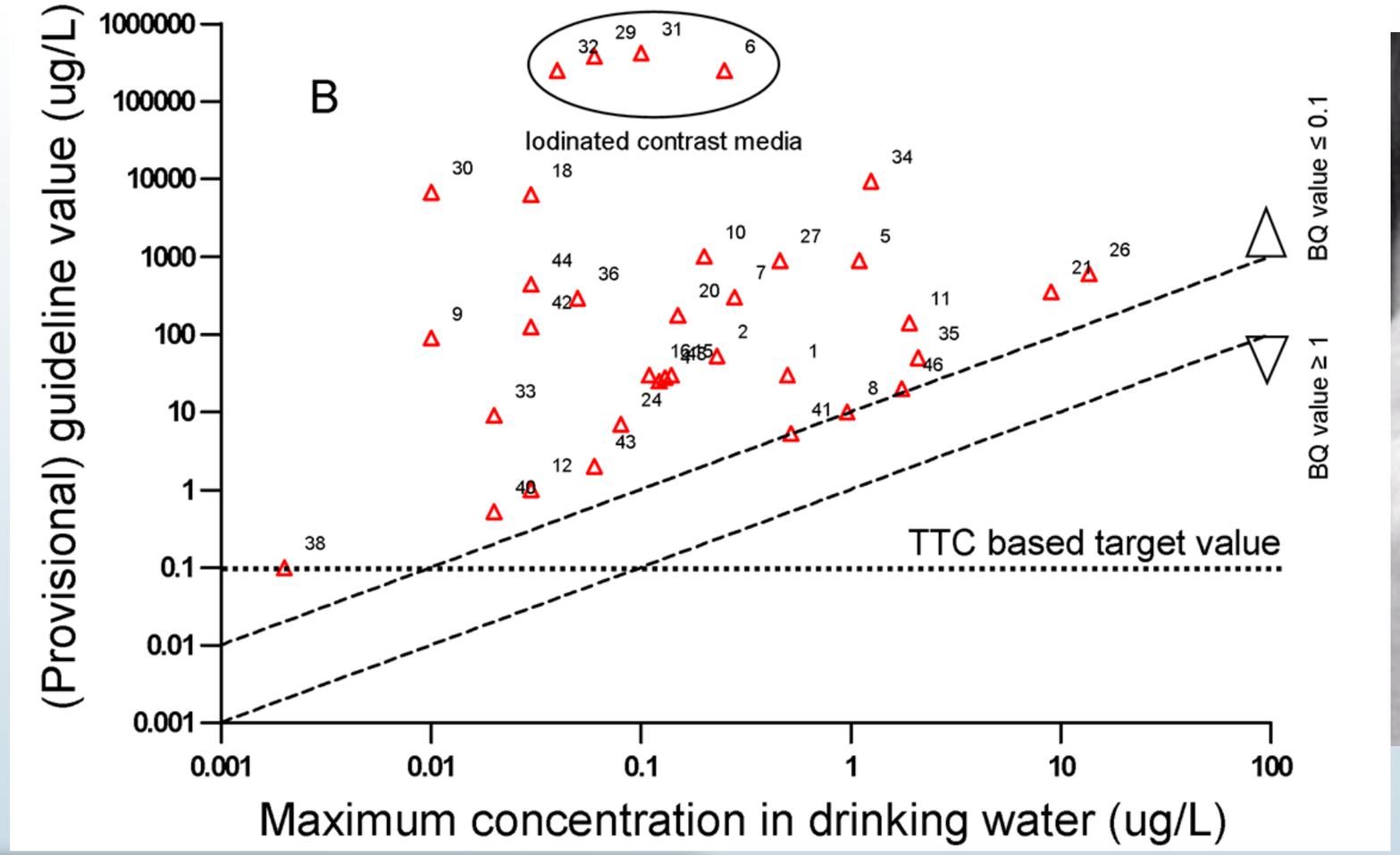


Sources: ACC and Cefic Chemdata International
* Asia includes Japan, China, Korea, Malaysia, Philippines, Singapore, Taiwan, Thailand, Pakistan, Bangladesh and Australia

Unless specified, chemicals industry excludes pharmaceuticals
Unless specified, EU refers to EU-27

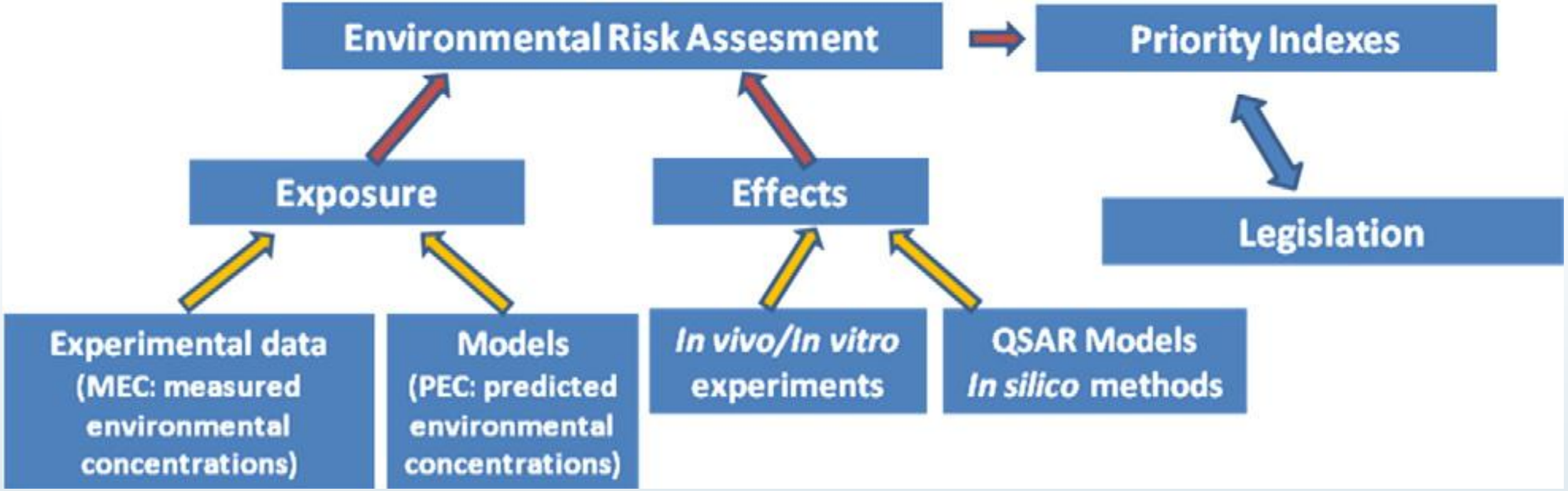
CHEMLIST: 308.000 substances on world market

For individual chemicals no human health risks expected – but mixtures



Schriks et al 2010

Various prioritization schemes exist…



…but hardly in context of drinking water
→ removal efficiency by water treatment
→ effects relevant for human health
→ where to intervene

Guillen et al 2012

Prioritization → research & risk assessment

$$\text{Score} = \frac{(\text{MON or FAT}) * \text{TE}}{\text{TA or HEA}}$$

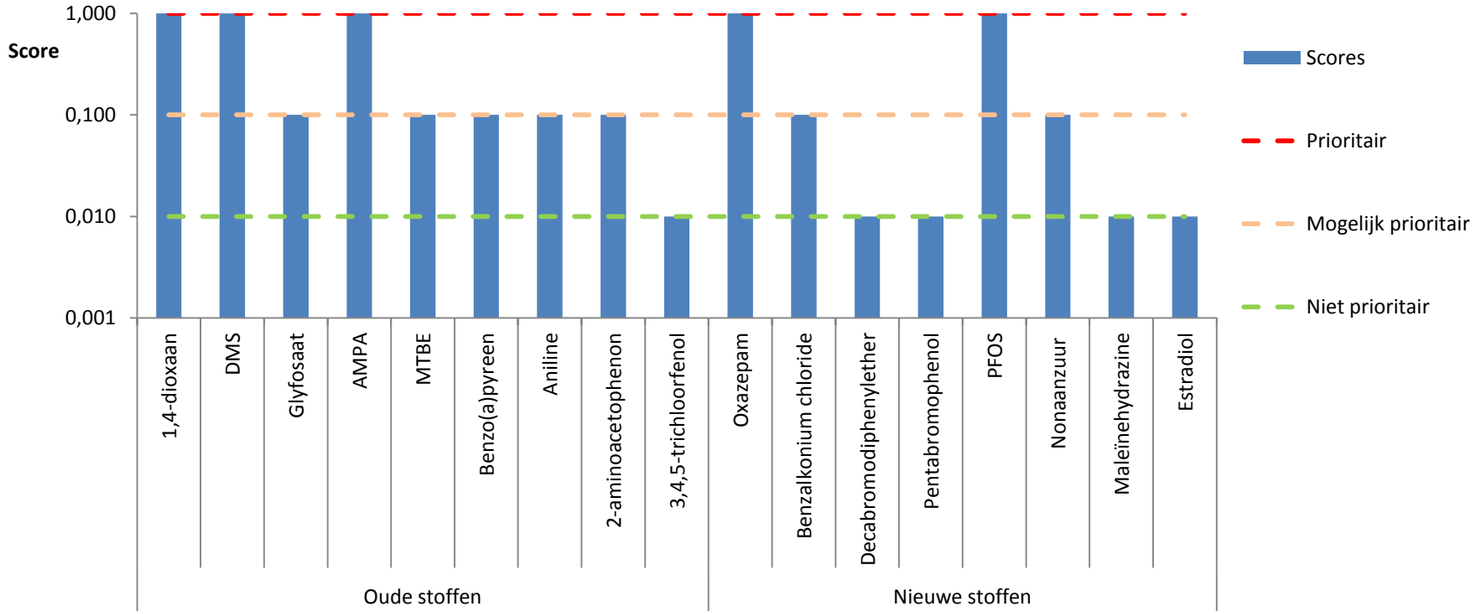
>1: priority

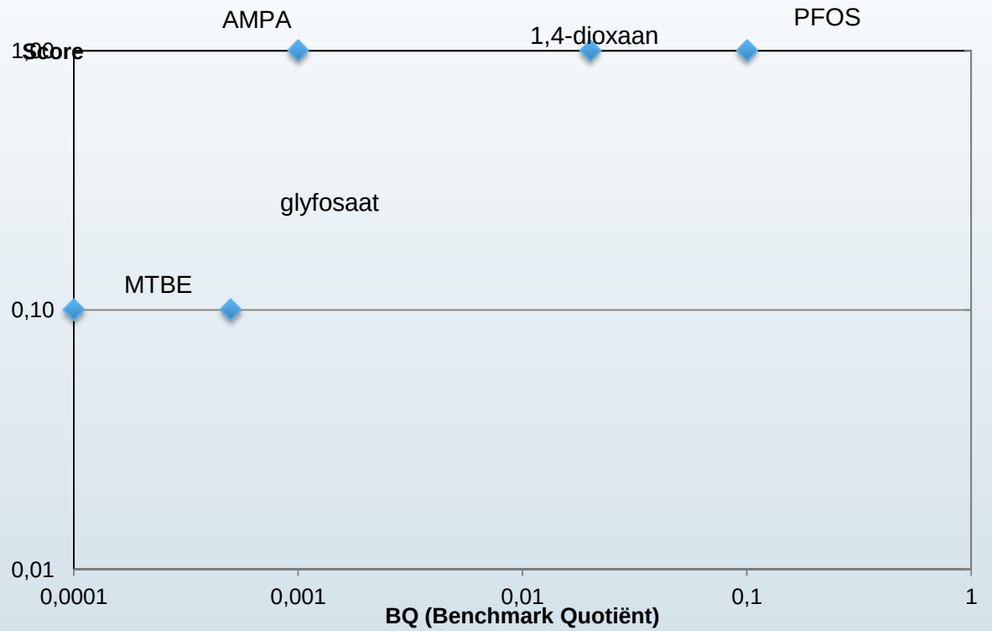
>0,1 : possibly priority

<0,01: non priority

		Class	Factor
MON	Mean water concentration	> 0,1 µg/L	1000
		0,01-0,1 µg/L	100
		0,001-0,01 µg/L	10
		< 0,001 µg/L	1
FAT	V*H*P		
	Volume (V)	HPVC	10
		other	1
	Hydrophobicity (H)	log K_{ow} < 4	10
		log K_{ow} > 4	1
	Persistence (P)	$T_{0,5}$ > 50 days	10
		$T_{0,5}$ < 50 days	1
TE		Occurs in drinking water	1
	GAC removal	log K_{ow} < 4	1
		log K_{ow} > 4	0.1
HEA	Based on TTC	Carcinogen or EDC	100
		other	1000
TA	Taste or odor limit	<TTC	100

Test compounds; System tested compared to data-rich risk assessment





Preselection → prioritization → risk assessment

Preselection based on measured or modeled (indicative) water concentration

Suspect analysis in context of prioritization…

Chemicals authorized on EU market
REACH
- HPVC
- SVHC
- CMR
- PBT

Human/veterinary pharmaceuticals
Pesticides / biocides (NL market)
WFD / DWD
Attention lists (Norman, IAWR, etc)

→ mol. form, mol. weight, K_{ow}, pKa for 6080 parent compounds

130 Dutch water samples, accurate mass, + ionization 2007-2013
20 drinking waters
39 ground waters
65 surface waters
6 STP effluents

Compare to EUSES modelled concentrations for REACH/pesticides/biocides

…work in progress…

Results on smaller scale:

1556 REACH HPVC, CMR and PBT compounds
2 surface waters, 5 STP effluents

in total **211 out of 1556** compounds observed

Sample	Number of confirmed elemental compositions	Total response in µg/L atrazine d_5 equivalents
STP 1 - Utrecht	82	**26.1**
STP 2 - Eindhoven	68	**21.1**
STP 3 - Amersfoort	65	**17.8**
STP 4 - Amsterdam	65	**15.0**
STP 5 - Schiphol	46	**31.2**
Surface water (Lek canal)	45	**1.5**
Surface water (Meuse Keizersveer)	**28**	**1.2**

-not inclusive to all chemicals (extraction, ionization, separation, blanks)

-analysis of standards enables definitive identification

Presumed chemical(s)	STP	SW	
1,3-diphenylguanidine	4	2	Observed in SW and STP effluents
3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate	5	1	
tris(2-chloro-1-methylethyl) phosphate	4	1	
3-(iso decyloxy)propiononitrile	2		
tris(2-butoxyethyl)phosphate	4	1	
tributylphosphate		2	
Dodecane nitrile or Dicyclohexylamine	1		
2,2'-[oxybis(methylene)]bis[2-ethylpropane-1,3-diol]	1		
2-butoxyethyl acetate	1		
5-allyl-1,3-benzodioxole	1		
N-[3-(dimethylamino)propyl] Methacrylamide		1	
dimethyl(tetradecyl)amine		1	
triphenylphospine oxide		2	
2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol or Alpha-2,2,6-tetramethylcyclohexene-1-butyraldehyde		2	
1,1',1”-nitrilotripropan-2-ol	4		Observed in STP effluents
1,1',1'',1'''-ethylenedinitrilotetrapropan-2-ol	4		
Cycloheximide	4		
Climbazole	2		
6,6'-di-tert-butyl-4,4'-thiodi-m-cresol	1		
Dacarbazine	1		
dibutyl fumarate or dibutyl maleate	4		
Benomyl	2		
heptanoic acid	1		
[2-(2-methoxymethylethoxy)methylethoxy]propanol or 2-(2-(2-butoxyethoxy)ethoxy)ethanol	1		
4,4'-bis(dimethylamino)-4''-(methylamino)trityl alcohol	1		
exo-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl methacrylate	1		
3-hydroxy-2,2-dimethylpropyl or 3-hydroxy-2,2-dimethylpropionate or 2-(2-butoxyethoxy)ethyl acetate	1		
(Z)-cyclooctene		2	Obs. In SW
hexyl D-glucoside		2	
2-nitroanisole		1	
tert-butyl perbenzoate		1	
dibutyl terephthalate or diisobutyl phthalate or dibutyl phthalate		1	

Combined ‘top tens’

32 out of the 211 compounds observed
Some in both STP and SW, some not

→ Compare concentration to TTC
→ QSARs treatment

Table 4 – Proposed target values for organic contaminants in drinking water.

Compound group	Target value (µg/L)
Single genotoxic organic chemicals	0.01
Single (synthetic) steroid hormones	0.01
All other single organic chemicals	0.1
Total sum of genotoxic compounds	0.01
Total sum of (synthetic) steroid hormones	0.01
Total sum of all other organic chemicals	1.0

QSARs for water treatment

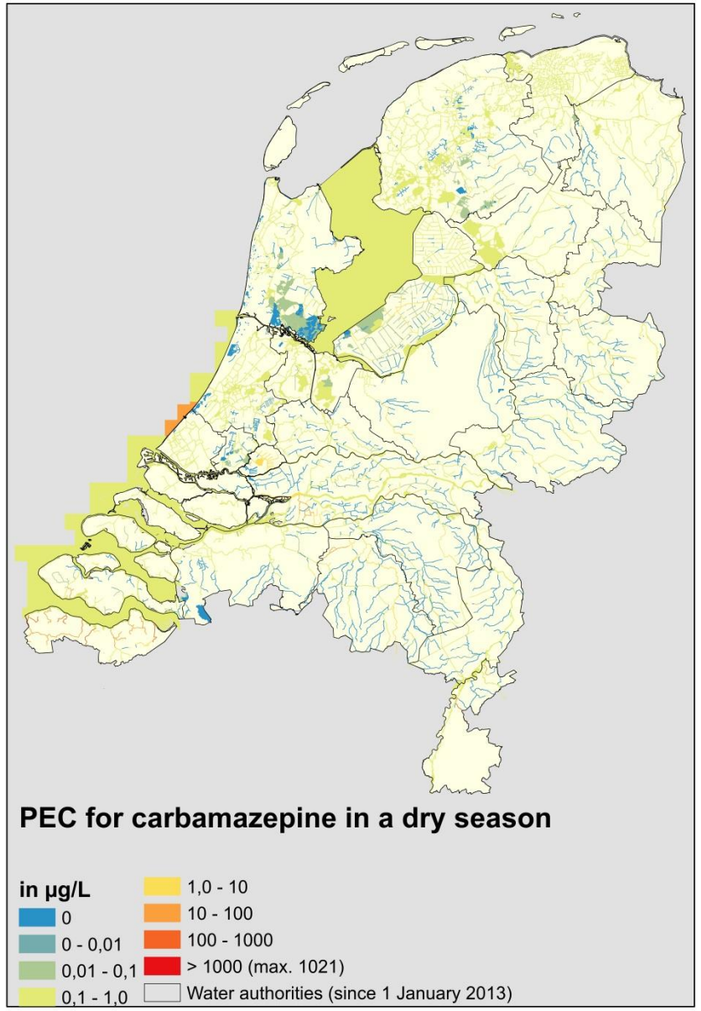
Review available QSARs for water treatment technologies;

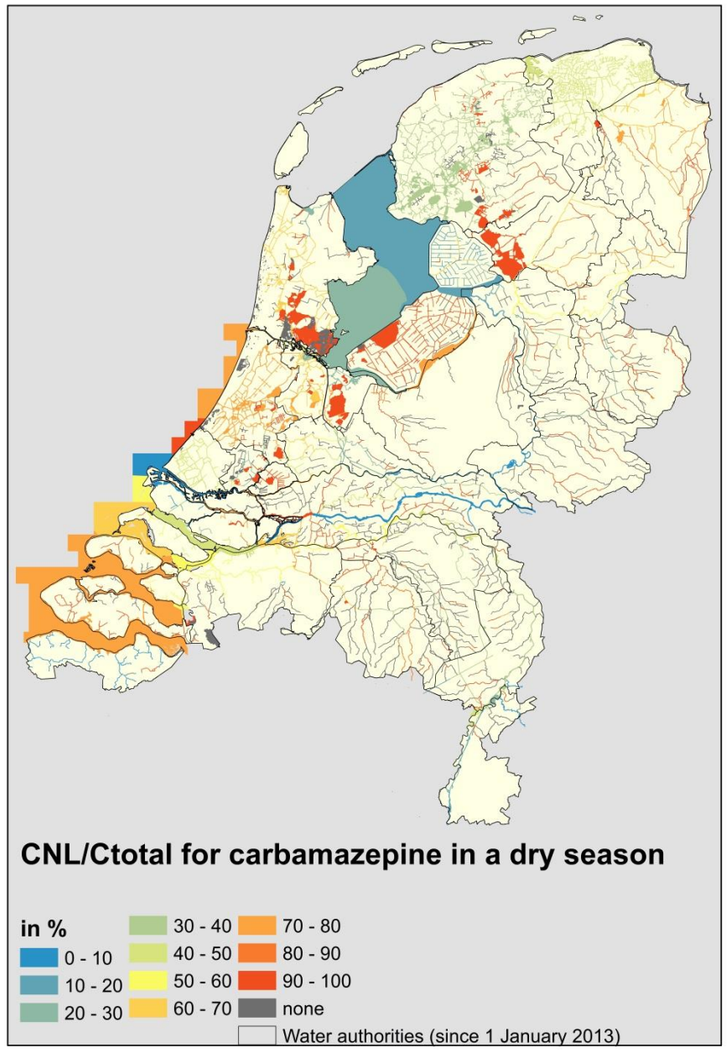
- technologies where sorption and biodegradation dominate
- where oxidation dominates
- where size exclusion processes dominate

→ r2, descriptors, nrs compounds, validation

→ Use weight of descriptors in prioritization

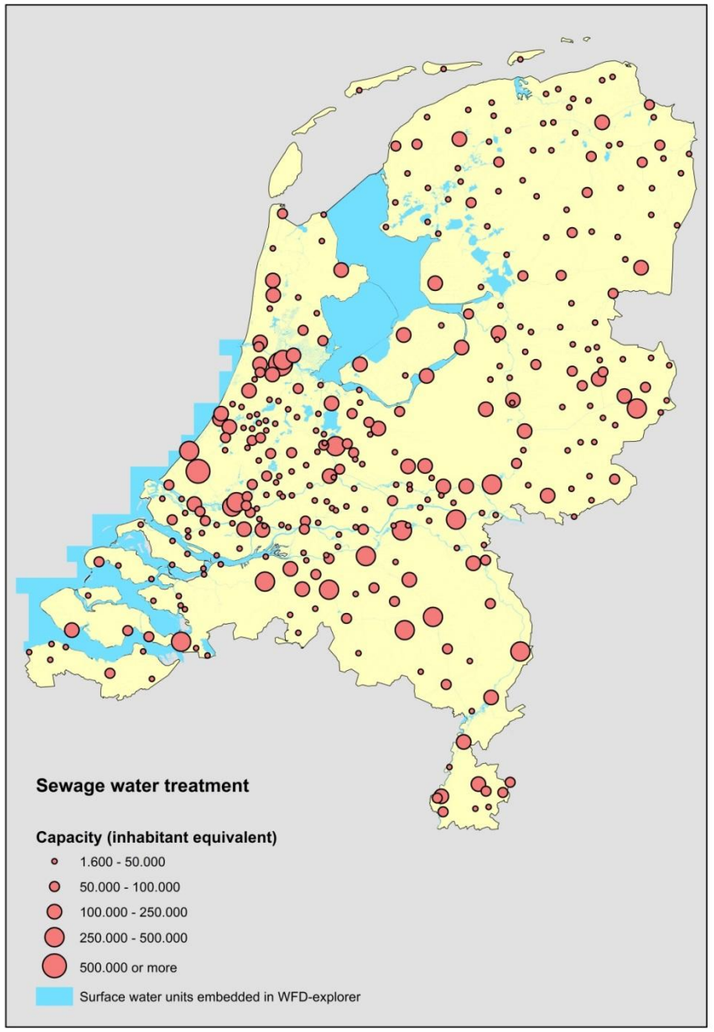
Where to intervene? (Preliminary results)

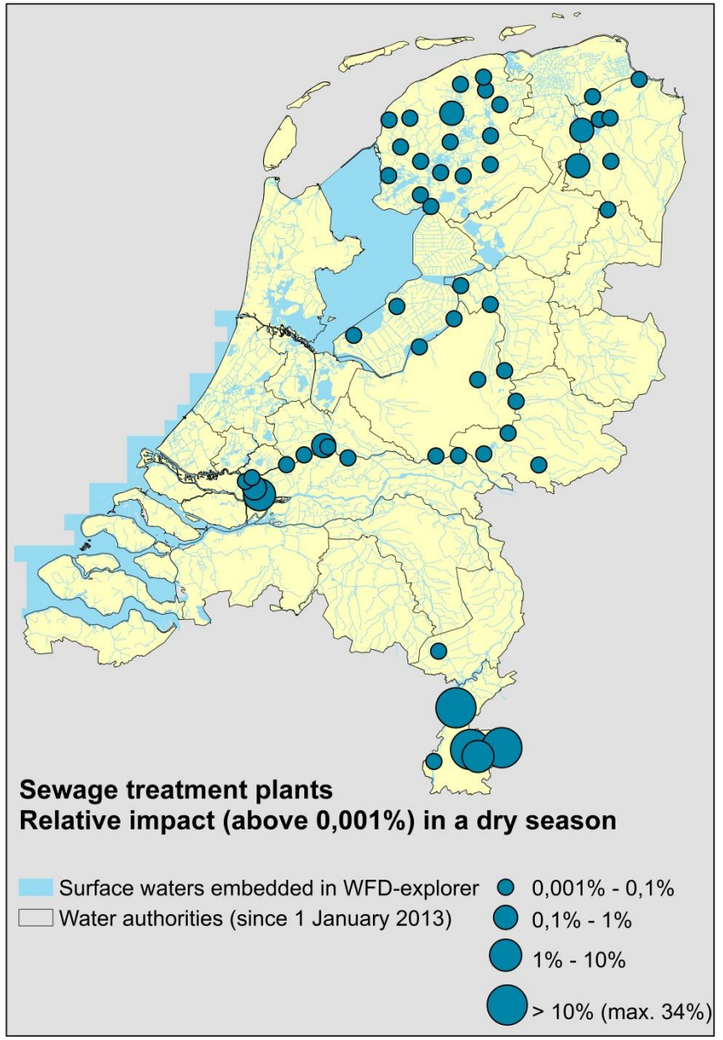


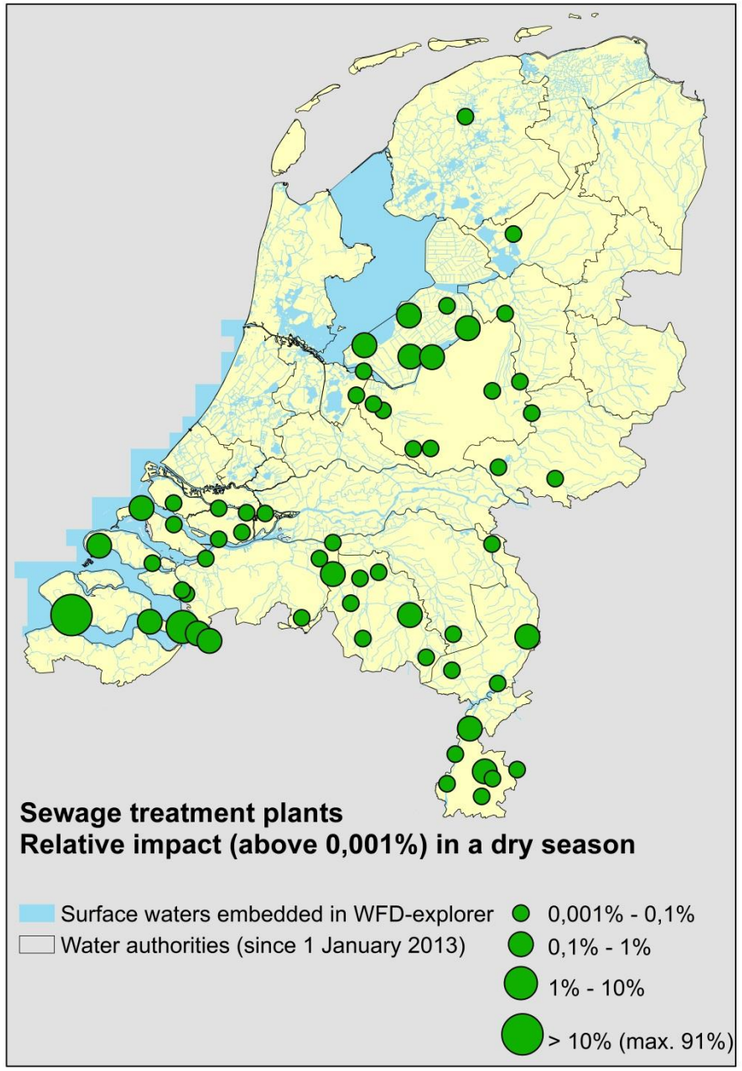


Drinking water extractions	n total	n (in contact with) surface water
Surface water	9	9
Bank filtrate	19	19
Groundwater A, A2, B and K	143	39
Groundwater B2	42	No contact assumed
Total	213	71

Impact per STP differs on function of watersystem (preliminary results)





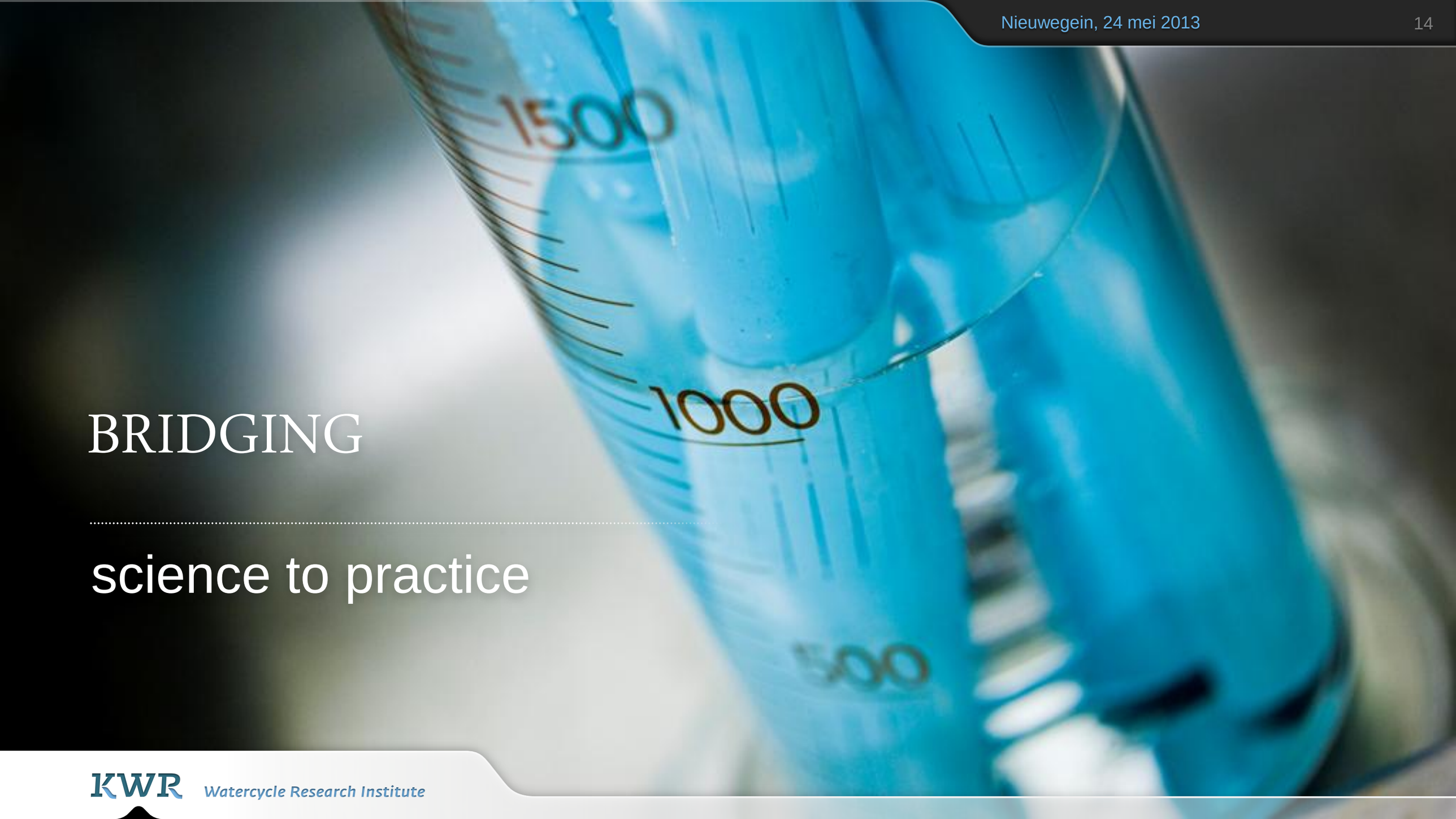


Future perspectives

Explicit coupling of authorisation per chemical to regulation of mixtures as environmentally occur

Regulation of mixtures of chemicals from characteristic sources (e.g. waste water effluents, typical industrial emissions, agricultural emissions, emission solid waste)

Spatially prioritize additional interventions



BRIDGING

science to practice