



Contaminants of Emerging Concern and Drinking Water Supply

International Water Days Symposium, Slovenia

7 October 2021

Jan Peter van der Hoek

Contaminants of Emerging Concern



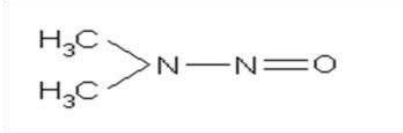
Pharmaceuticals



Perfluor compounds



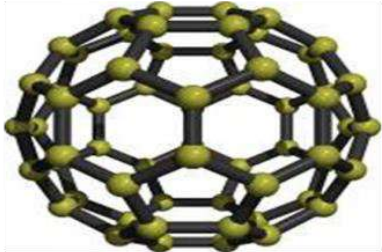
Endocrine disruptors



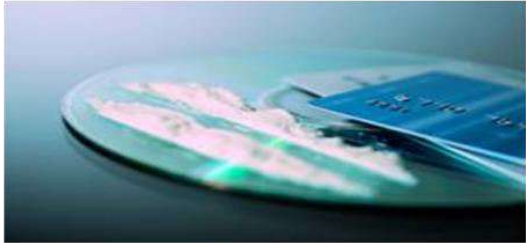
NDMA



Pesticides

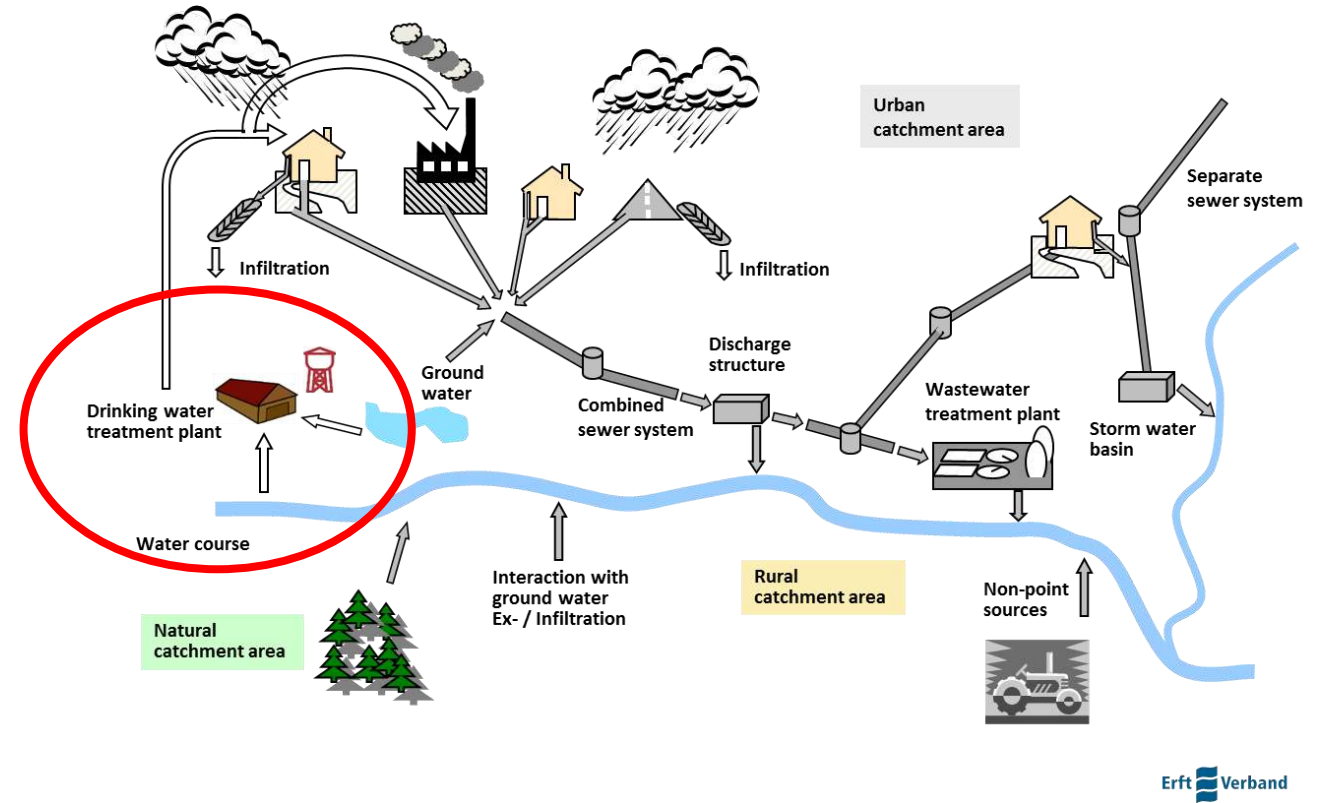
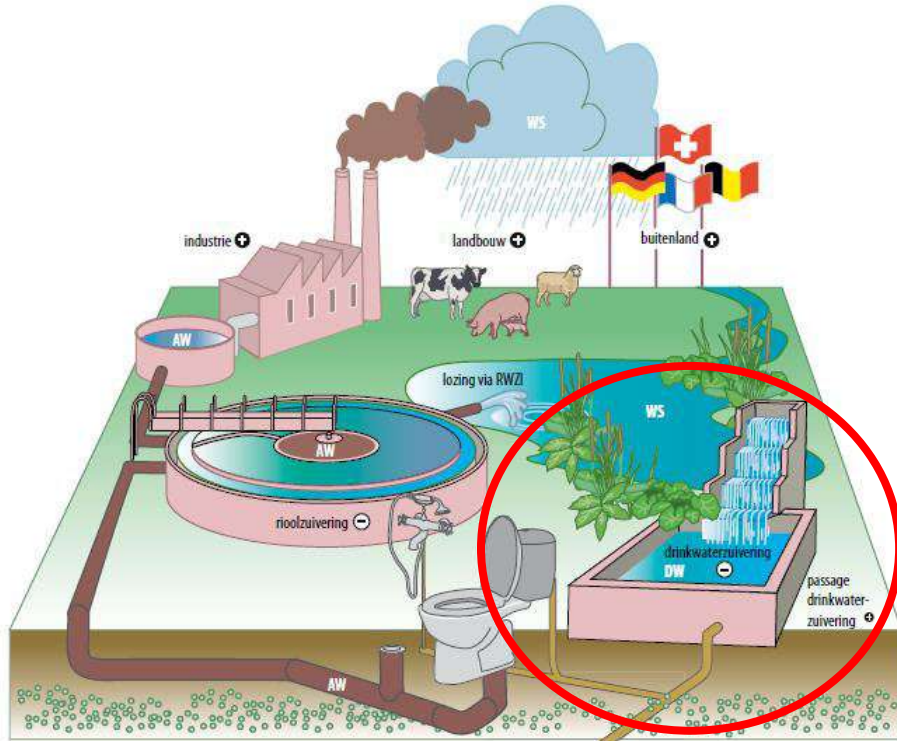


Nanochemicals



Drugs of abuse

Presence in the water cycle



Resource protection

- Water Framework Directive:
 - “[..] avoiding deterioration in their quality to reduce the level of purification treatment [..]” Art. 7 (3)
- European Drinking Water Directive:
 - “[..] Member States shall ensure that risk assessment and risk management of the catchment areas for abstraction points of water intended for human consumption is carried out.” Art. 8 (1)

Drinking water treatment technologies in Europe

- Raw water sources:
- Groundwater
 - Surface water
 - Surface water + AR
 - River bank filtration

- Treatment schemes:
- No treatment
 - Conventional treatment
 - Advanced treatment
 - Conventional + advanced treatment

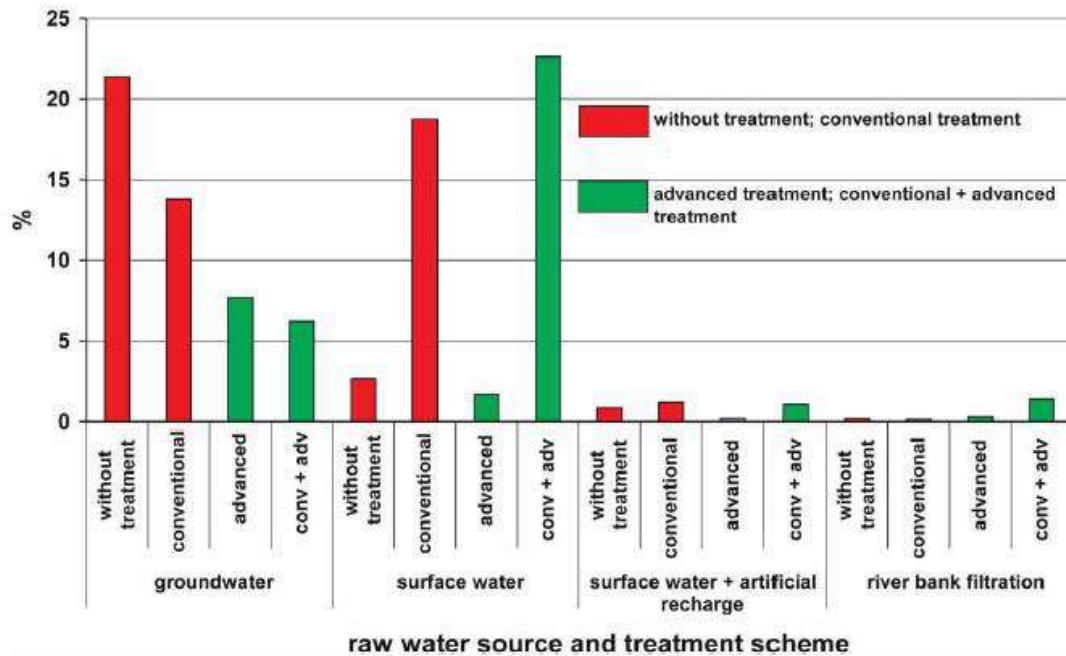
		Raw water source			
		Groundwater	Surface water	Surface water + artificial recharge	River bank filtration
Treatment scheme	No treatment	-	-	surface water + AR ³ without treatment	no post treatment
	Conventional treatment	aeration and/or RSF ¹	CSF ²	surface water + AR ³ with treatment: aeration and/or CSF	post treatment: aeration and/or RSF ¹
	Advanced treatment	carbon filtration, AOP ⁴ , membranes, desalination, etc.	carbon filtration, AOP ⁴ , membranes, desalination, etc.	surface water + AR ³ with treatment: advanced treatment like carbon filtration, AOP ⁴ , membranes, desalination, etc.	post treatment: carbon filtration, AOP ⁴ , membranes, desalination, etc.
	Conventional + advanced treatment	aeration and/or RSF ¹ + advanced treatment	CSF ² + advanced treatment	surface water + AR ³ with treatment: aeration and/or CSF ² + advanced treatment	post treatment: aeration and/or RSF ¹ + advanced treatment

¹Rapid Sand Filtration; ²Coagulation/Sedimentation/Filtration; ³Artificial Recharge; ⁴Advanced oxidation Processes

16 systems

Drinking water treatment technologies in Europe

Van der Hoek et al., Journal of Water Supply: Research and Technology-AQUA 63.2 (2014), 124-130



Process	Emerging contaminant															
	1,4-dioxaan	amido-trizomezuur	atrazine	benzeen	bisphenol-A	carbamazepine	diethylfalaat	diglyme	lopamidol	MTBE	NDMA	PFOA	PFOS	TBA	TCEP	triglyme
RO	Green	Green	Green	Red	Green	Green	Green	Yellow	Green	Green	Red	Green	Green	Red	Green	Green
O ₃ + BACF	Red	Green	Green	Green	Green	Green	Green	Green	Green	Red	Green	Green	Green	Red	Green	Green
UV + H ₂ O ₂ + BACF	Orange	Green	Green	Green	Green	Green	Green	Green	Green	Red	Green	Green	Green	Red	Green	Green

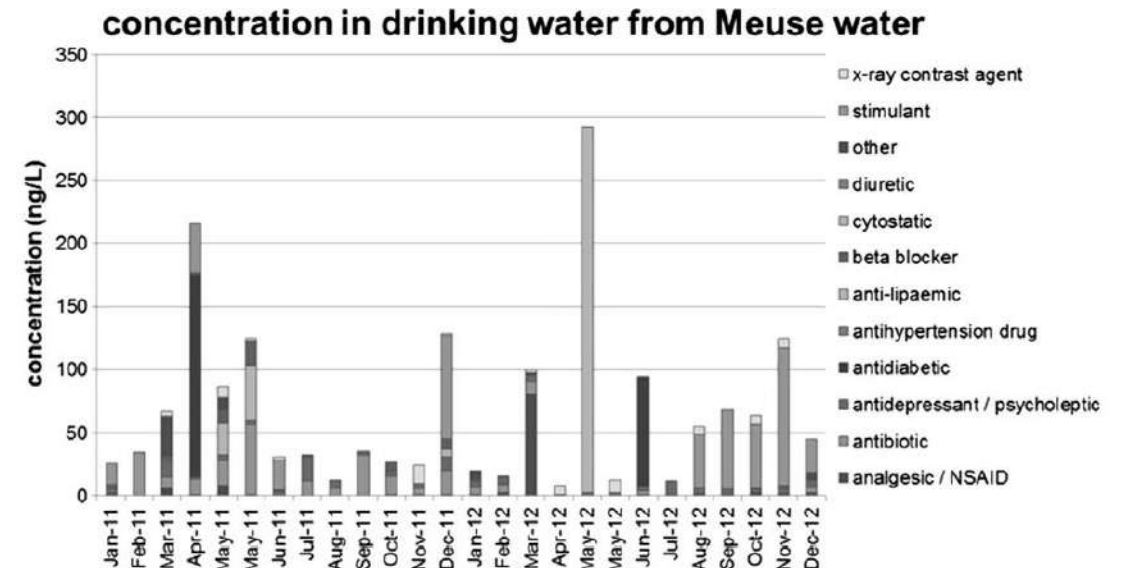
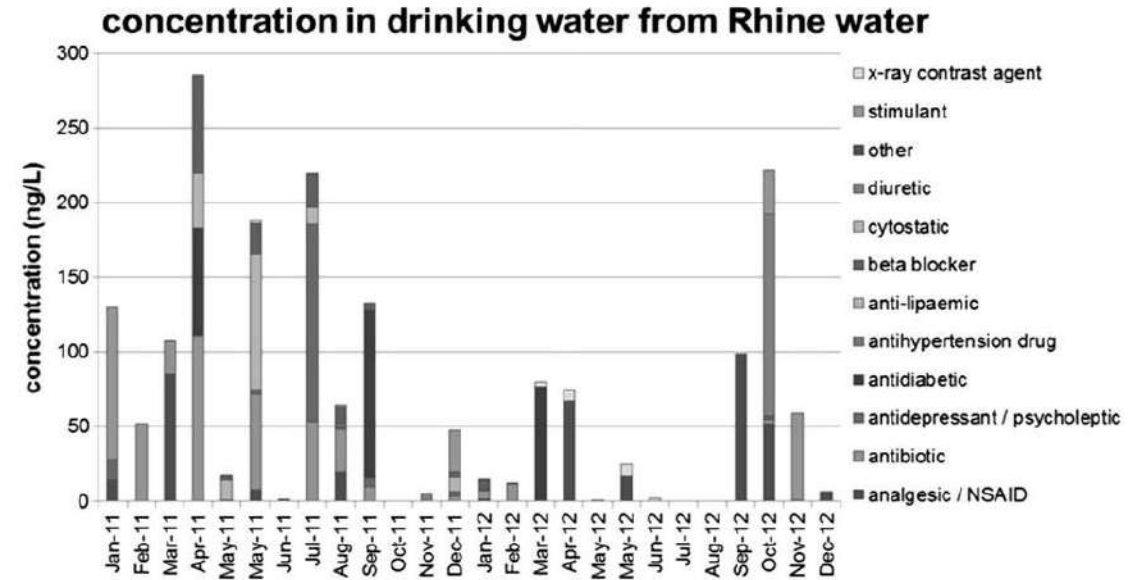
Removal/conversion:

■ = poor (0-40%)
 ■ = moderate (40-60%)
 ■ = good (60-80%)
 ■ = very good (80-100%)

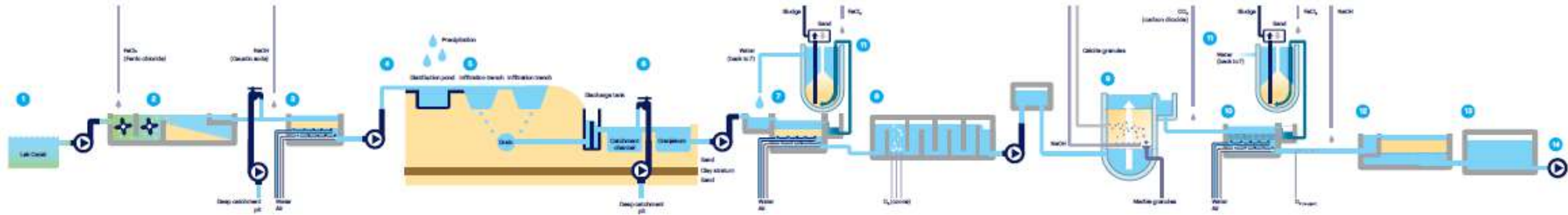
Pharmaceuticals in Dutch drinking water and its sources Rhine and Meuse

- 2-year set of 4-weekly monitoring data of pharmaceuticals (2011-2012)
- 42 pharmaceuticals monitored
- 37 pharmaceuticals detected
- Lifelong exposure < 10% of 1 DDD

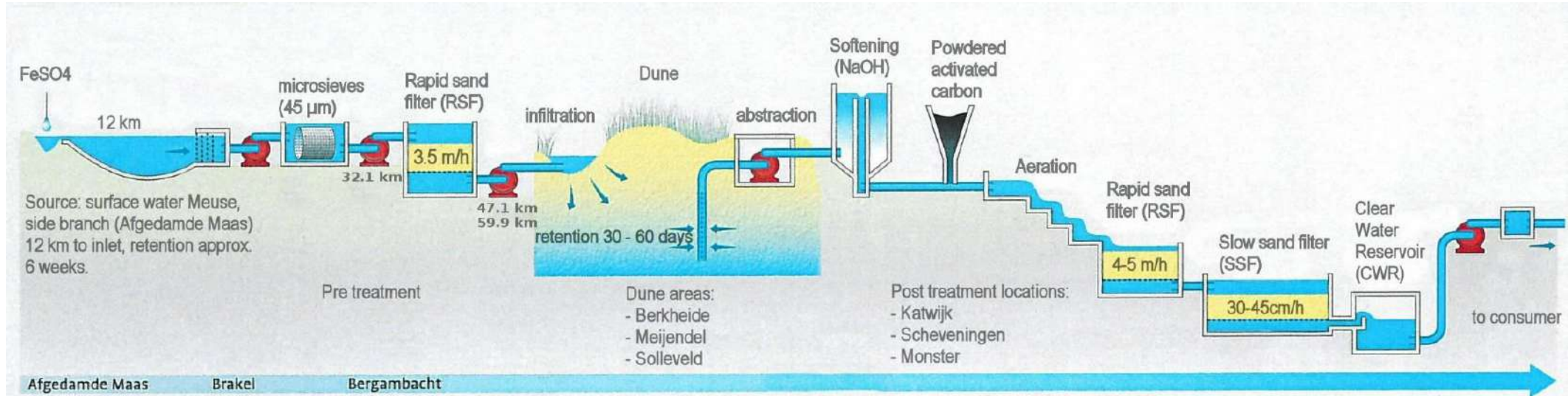
Houtman et al., Science of the Total Environment 496 (2014), 54-62



River Rhine: advanced treatment



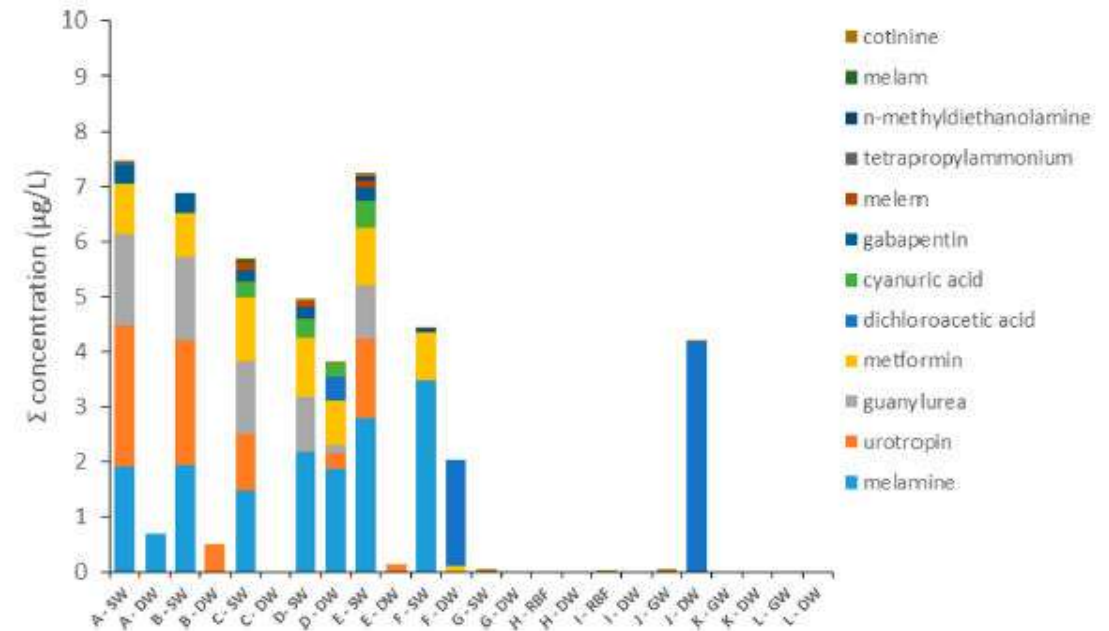
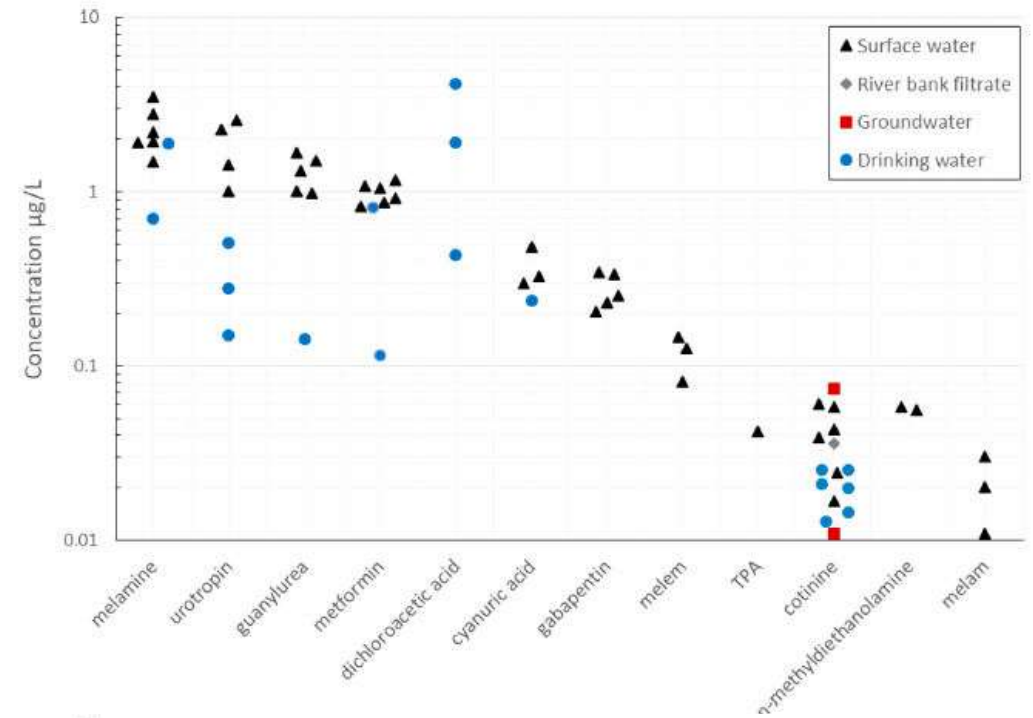
River Meuse: advanced treatment



Highly polar chemicals in Dutch and Flemish drinking water and its sources

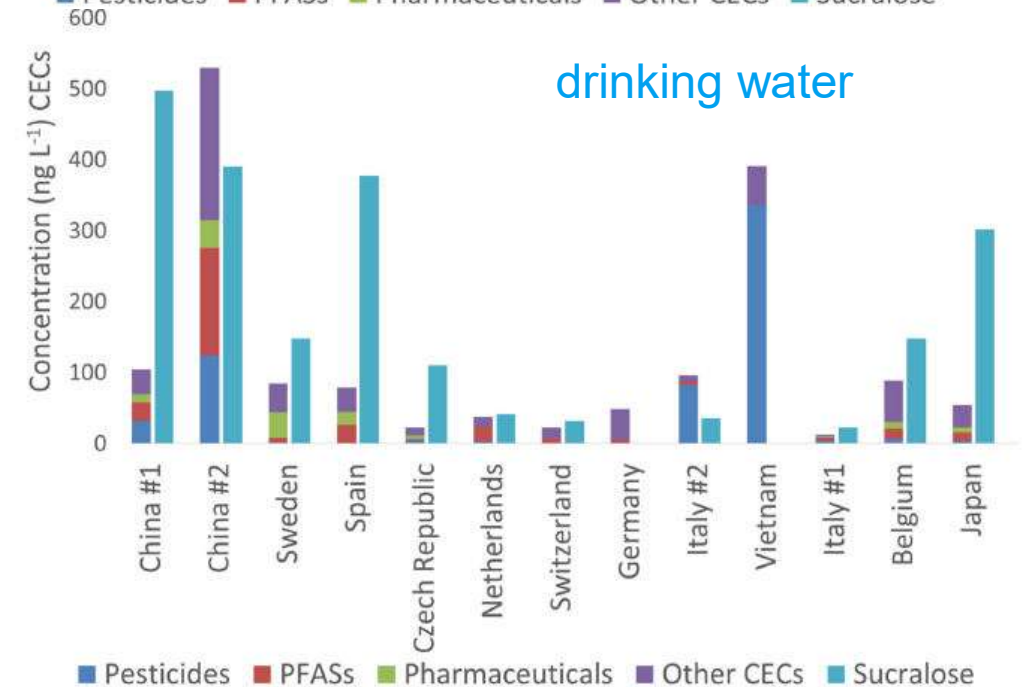
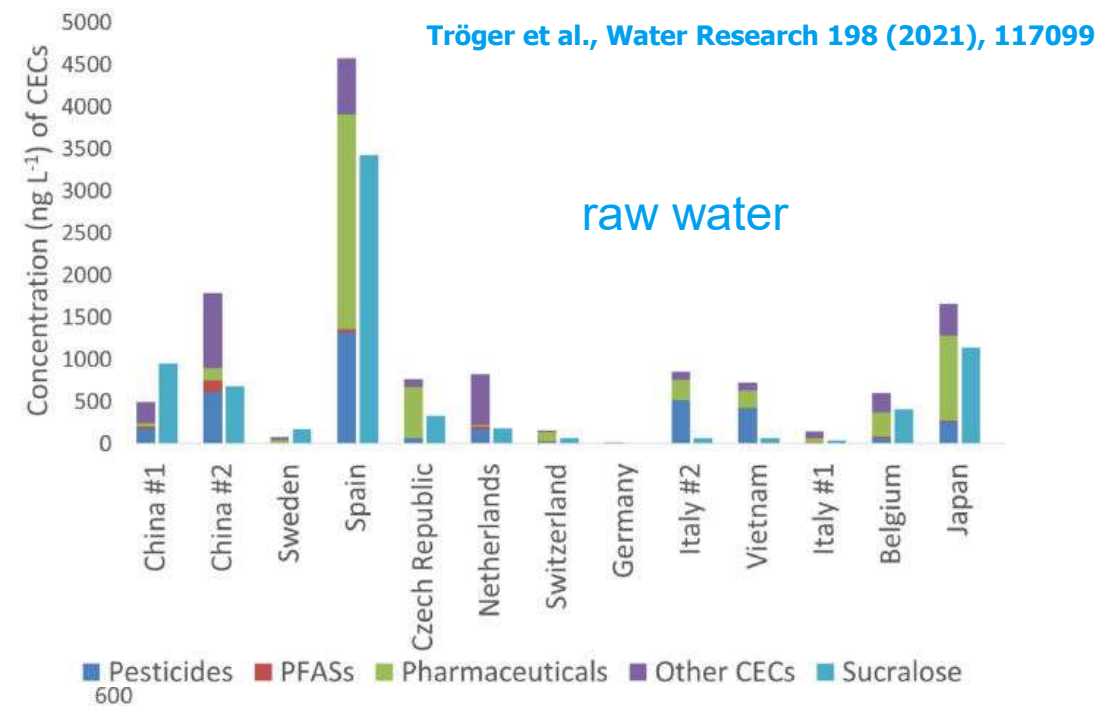
- 32 persistent mobile organic contaminants (PMOCs) analysed
- 12 compounds detected in groundwater, surface water and drinking water
- Levels between 0.01 and 4.2 µg/L
- One compound above pGLV

(dichloroacetic acid)



CECs in raw water and drinking water from Europe and Asia

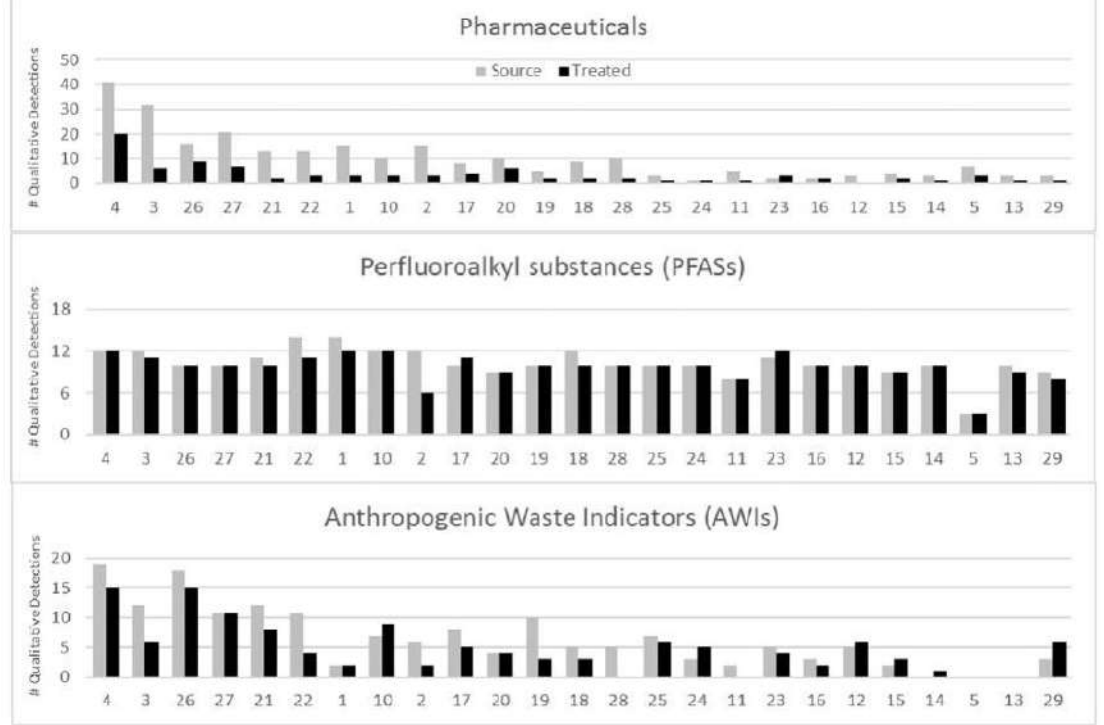
- 13 DWTPs (9 European, 4 Asian)
- Use of surface water
- Pharmaceuticals, pesticides, PFASs, other compounds
- 115 out of 177 target compounds detected
- Raw water 15-7795 ng/L
- Drinking water 35-919 ng/L
- Treatment efficiency $65 \pm 28\%$



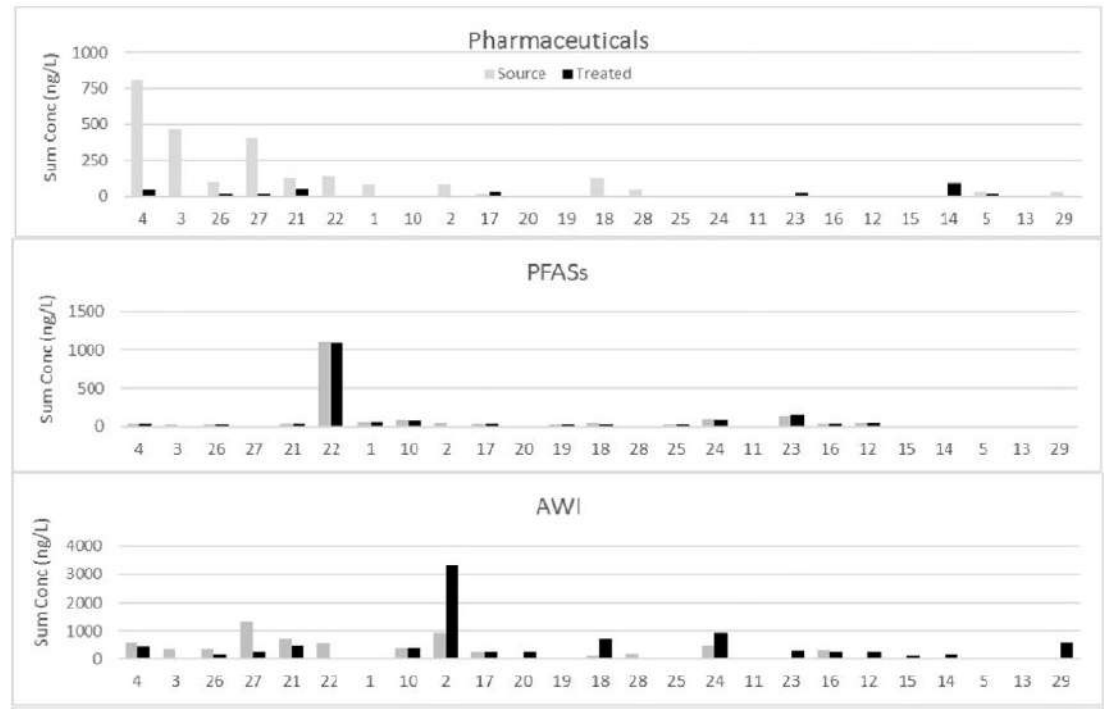
CECs in source and treated drinking waters of the USA

- 29 DWTPs
- Phase I (2007), 84 chemicals monitored
 - 27 detected in source water
 - 21 detected in treated drinking water
- Phase II (2010-2012), 247 chemicals monitored
 - 148 detected in source water
 - 121 detected in treated drinking water

Qualitative detections



Concentrations

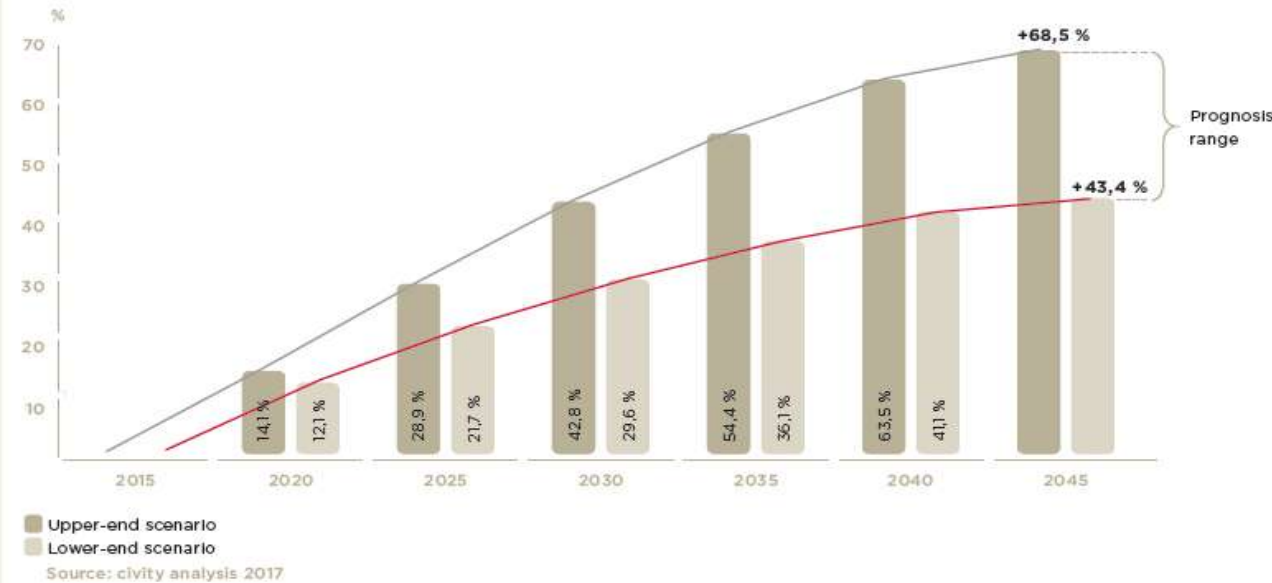


Some general observations

- A wide variety of CECs are present in raw water sources and in drinking water, even with advanced drinking water treatment schemes
- Many CECs are not regulated: neither in raw water sources nor in drinking water
- Pharmaceuticals show no health issue in drinking water, but the problem may grow

Predicted use of pharmaceuticals

GROWTH PROGNOSIS FOR THE CONSUMPTION OF PRESCRIPTION DRUGS FOR HUMAN USE



- Situation is likely to deteriorate in the future
- Pharmaceuticals in the environment pose a threat to the aquatic environment and drinking water resources

Predicted use of pharmaceuticals

Table 1 | Forecast of consumption of 33 selected pharmaceuticals, based on projections of demographic changes in the Dutch population between 2007 and 2050. Results are given per pharmaceutical group

Pharmaceutical group	Consumption 2007 (kg)	Consumption 2020 (kg)	Consumption 2050 (kg)	Total growth % 2007–2020	Total growth % 2007–2050
Antidiabetics ¹	230.211	284.559	296.737	24	29
Analgesics ²	133.976	163.489	224.916	22	68
Heart and cardiovascular ³ (antihypertensives/ lipid modifying agents)	70.613	87.418	96.245	24	36
Antirheumatics ⁴	51.758	55.387	55.963	7	8
Antiinfectives/antibiotics ⁵	33.754	36.719	40.201	9	19
Antiepileptics ⁶	21.675	23.891	24.557	10	13
Gastrointestinal drugs ⁷	7.827	9.239	10.094	18	29
Antigout preparations ⁸	4.430	5.544	6.096	25	38
Antidepressants/tranquiliser ⁹	665	747	1.071	12	61
Anticancer drugs ¹⁰	19	23	23	19	18
Sex hormones/estrogens ¹¹	16	16	15	-3	-6
Total	554.945	667.032	755.917	20	36

Some general observations

- A wide variety of CECs are present in raw water sources and in drinking water, even with advanced drinking water treatment processes
- Many CECs are not regulated: neither in raw water sources nor in drinking water
- Pharmaceuticals show no health issue in drinking water, but the problem may grow
- PFASs (perfluoroalkyl substances and polyfluoroalkyl substances) are hardly removed

PFAS regulation

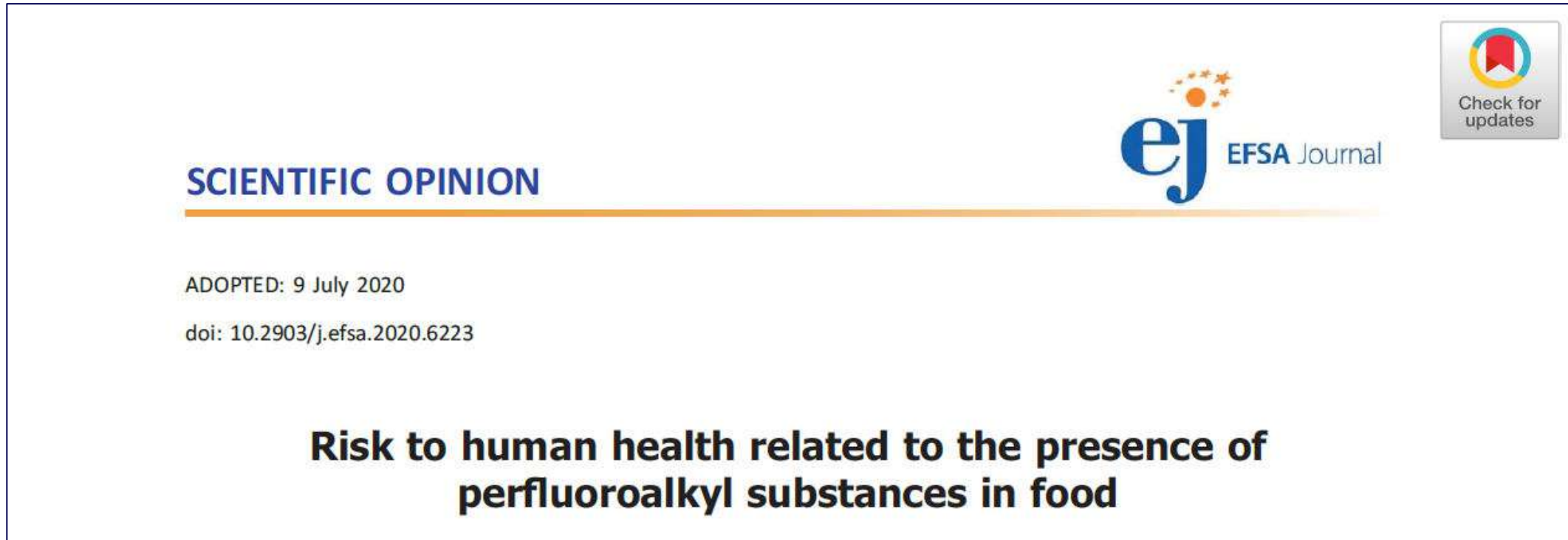
- New European Drinking Water Directive – January 2021

Parameter	Parametric value	Unit	Notes
PFAS Total	0.50	µg/L	'PFAS Total' means the totality of per- and polyfluoroalkyl substances
Sum of PFAS	0.10	µg/L	'Sum of PFAS' means the sum of per- and polyfluoroalkyl substances considered a concern as regards water intended for human consumption (20 specific PFASs)

PFAS regulation

- European Food Safety Agency – Scientific opinion 17 September 2020

4.4 ng/kg bodyweight/week for Σ PFOS, PFOA, PFNA and PFHxS



The image shows the cover of a scientific opinion document from the EFSA Journal. The title is "SCIENTIFIC OPINION" in blue, underlined with an orange line. Below it, the text reads "ADOPTED: 9 July 2020" and "doi: 10.2903/j.efsa.2020.6223". The main title of the opinion is "Risk to human health related to the presence of perfluoroalkyl substances in food". The EFSA Journal logo is in the top right, and a "Check for updates" button is also present.

SCIENTIFIC OPINION

ADOPTED: 9 July 2020
doi: 10.2903/j.efsa.2020.6223

Risk to human health related to the presence of perfluoroalkyl substances in food

ej EFSA Journal

Check for updates

PFAS-EFSA health-based guideline value (HBGV) for drinking water

$$HBGV = \frac{\textit{Tolerable Daily intake} \times \textit{standard body weight} \times \textit{allocation}\%}{\textit{Daily consumption of drinking water}}$$

- TDI = 4.4 ng/ kg bw/w / 7 days = 0.63 ng kg bw /day
- Bodyweight 70 kg
- Drinking water consumption 2 L/day
- Allocation drinking water 20%

$$HBGV = \frac{\textit{Tolerable Daily intake} \times \textit{standard body weight} \times \textit{allocation}\%}{\textit{Daily consumption of drinking water}} = 4.4 \text{ ng/L PFOA equivalents}$$

Relative Potency Factor: Concentrations are translated to PFOA- equivalents

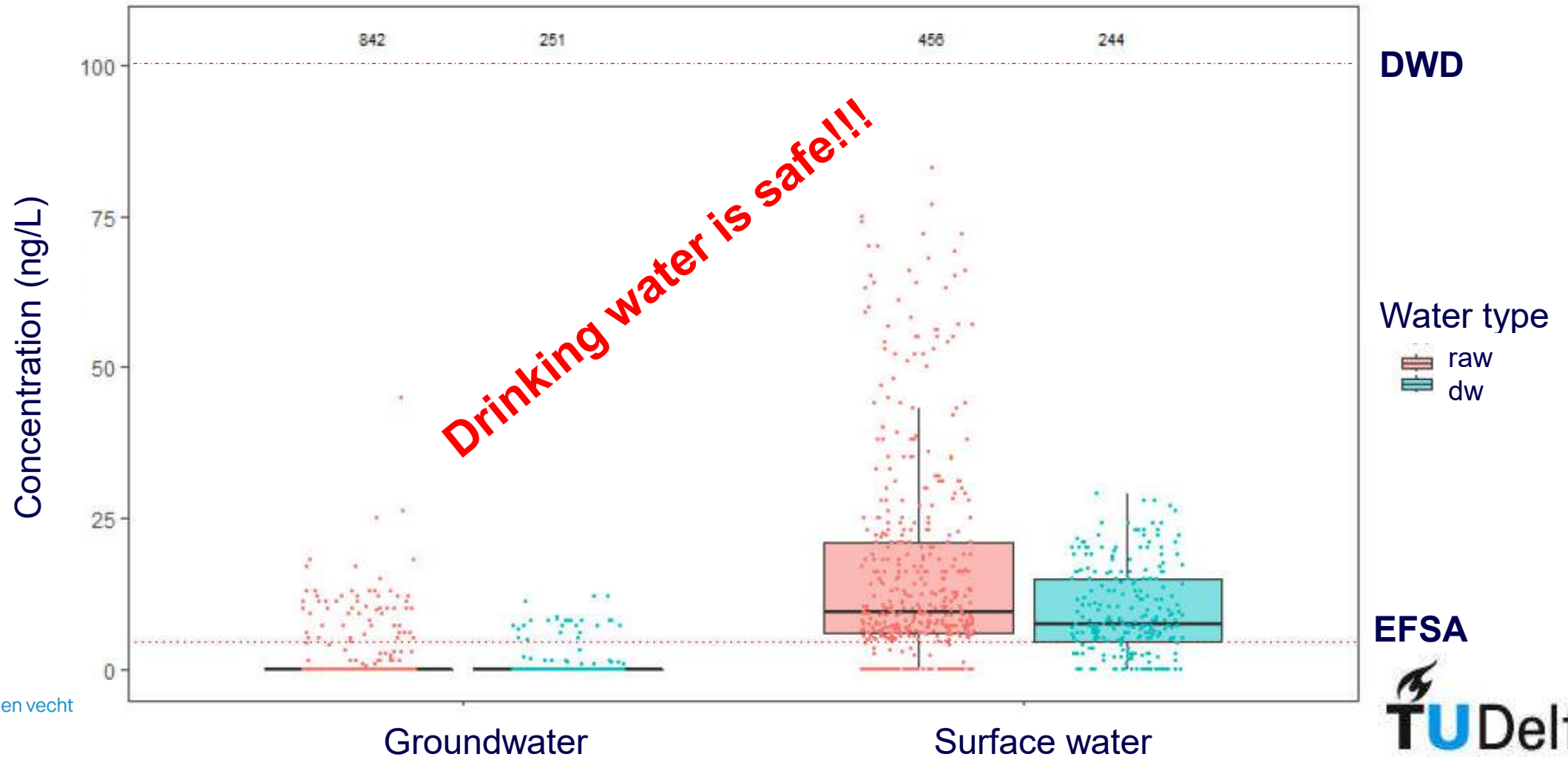
Compound	Name	Concentration (ng/L)	RPF factor	PFOA equivalents (PEQ) (ng/L)
PFOA	Perfluorooctanoic acid	1	1	1
PFOS	Perfluorooctane sulfonic acid	1	2	2
PFNA	Perfluorononanoic acid	1	10	10
PFHxS	Perfluorohexane sulfonic acid	1	0.6	0.6
		$\Sigma = 4$		$\Sigma = 13.6$

DWD-PFAS versus EFSA-PFAS

DWD	EFSA
100 ng/L as Sum of 20 PFAS compounds	4.4 ng/L as PFOA-equivalents for 4 PFAS compounds

Removal efficiency drinking water treatment – an example

Total 4 PFAS, 2019-2020



Limited effect



Effective...but very expensive!



Compound	n	Min	Max	Average removal %	Passage %
1,4-Dioxane	2	89.7	91.1	90.4	9.6
1H-Benzotriazole	2	8.2	27.7	15.6	84.4
2,4-D	4	99.6	99.8	99.7	0.3
4-Methyl-1H-benzotriazole	6	14.0	64.8	38.7	61.3
5-Methyl-1H-benzotriazole	6	8.7	45.7	24.4	75.6
Acesulfame-K	6	98.1	99.9	99.6	0.4
Aniline	2	47.3	70.0	59.1	40.9
Atrazine	6	99.1	99.7	99.4	0.6
Barbital	2	91.7	94.3	93.1	6.9
Bentazone	2	99.3	99.4	99.3	0.7
Benzene	2	8.3	21.7	13.7	86.3
Bisphenol A	2	98.5	98.9	98.7	1.3
Bisphenol S	6	97.1	99.7	98.5	1.5
Carbamazepine	8	97.1	99.9	98.9	1.1
Carbendazim	4	75.0	81.9	80.1	19.9
Chloridazon	4	83.7	95.6	91.3	8.7
Chlorotoluron	4	85.3	95.9	92.0	8.0
DEP	2	94.9	95.8	95.3	4.7
Dinatrioate	2	99.2	99.3	99.2	0.8
Dinatrioic acid	2	99.4	99.6	99.5	0.5
Diclofenac	8	82.3	88.1	85.9	4.1
Diglyme	2	62.5	64.2	63.4	36.6
Dimethenamid	4	99.2	99.7	99.5	0.5
Dimethomorph	2	99.2	99.5	99.4	0.6
Diuron	4	77.6	93.4	87.1	12.9
DNOC	2	97.6	99.7	99.2	0.8
Erythromycin	2	98.8	99.0	98.9	1.1
Estrone	2	97.2	99.4	98.8	1.2
ETBE	2	96.4	96.5	96.5	3.5
Furosemide	2	96.5	99.2	98.9	1.1
Gabapentin	2	98.5	98.5	98.5	1.5
Guanylurea	4	16.3	26.1	20.75	79.25
HFPO-DA	2	98.6	99.2	98.9	1.1
HMMM	2	93.2	93.8	93.5	6.5
Hydrochlorothiazide	2	92.8	96.5	95.0	5.0
Ibuprofen	2	99.1	99.2	99.1	0.9
Iopamidol	2	97.9	98.3	98.1	1.9
Isoproturon	4	95.7	99.0	97.9	2.1
MCPA	2	99.3	99.3	99.3	0.7
MCTP	2	99.3	99.4	99.4	0.6
Melamine	2	55.3	70.0	62.9	37.1
Metamitron	2	80.3	81.5	80.9	19.1
Metformin	6	74.5	87.3	83.1	16.9
Methenamine	2	96.4	99.1	98.2	1.8
Metoprolol	6	92.7	97.4	95.5	4.5
Metribuzin	2	98.9	99.0	98.9	1.1
MTBE	2	95.4	95.4	95.4	4.6
Naphthalene-1,3,6-trisulfonic acid	2	99.6	99.7	99.7	0.3
Naphthalene-1,5-disulfonic acid	2	99.5	99.6	99.6	0.4
NDMA	2	4.3	6.5	5.3	94.7
Nicosulfuron	4	99.6	99.8	99.7	0.3
NMOR	2	99.7	99.8	99.8	39.5
NTA	2	99.8	99.8	99.8	0.2
Nitroxyflin	4	94.7	99.3	98.4	1.6
PFBA	4	99.1	99.9	99.8	0.2
PFBS	4	98.8	99.5	99.2	0.8
PFHA	4	99.3	99.5	99.5	0.5
PFHS	4	99.3	99.5	99.4	0.6
PFNA	4	97.9	99.7	99.1	0.9
PFOA	6	99.3	99.6	99.5	0.5
PFOA	6	99.5	99.6	99.5	0.5
PFOA	6	99.5	99.6	99.5	0.5
Phenobarbital	2	96.0	97.3	96.7	3.3
Primicarb	2	99.5	99.7	99.6	0.4
Propranolol	2	86.2	93.8	90.3	9.7
Pyrazole	2	8.8	37.3	19.3	80.7
S-Metolachlor	4	99.7	99.8	99.8	0.2
Sotalol	6	94.7	98.1	96.6	3.4
Sucralose	2	91.9	94.6	93.4	6.6
Sulfamethoxazole	2	99.2	99.3	99.2	0.8
TBA	2	14.5	20.9	17.5	82.5
TCEP	2	98.1	98.5	98.3	1.7
Terbutylazine	2	98.5	99.0	98.8	1.2
Tetraglyme	2	85.2	88.6	87.0	13.0
TFA	2	97.3	98.2	97.8	2.2
Tiamulin	2	99.4	99.7	99.6	0.4
TPPO	2	99.2	99.3	99.2	0.8
Tramadol	2	97.0	98.2	97.7	2.3
Triglyme	2	80.6	83.2	81.9	18.1

Compound

n

Min

Max

Average

removal %

PFBA

4

99.1

99.9

99.8

PFBS

4

98.8

99.5

99.2

PFHA

4

99.3

99.5

99.5

PFHS

4

99.3

99.5

99.4

PFNA

4

97.9

99.7

99.1

PFOA

6

99.3

99.6

99.5

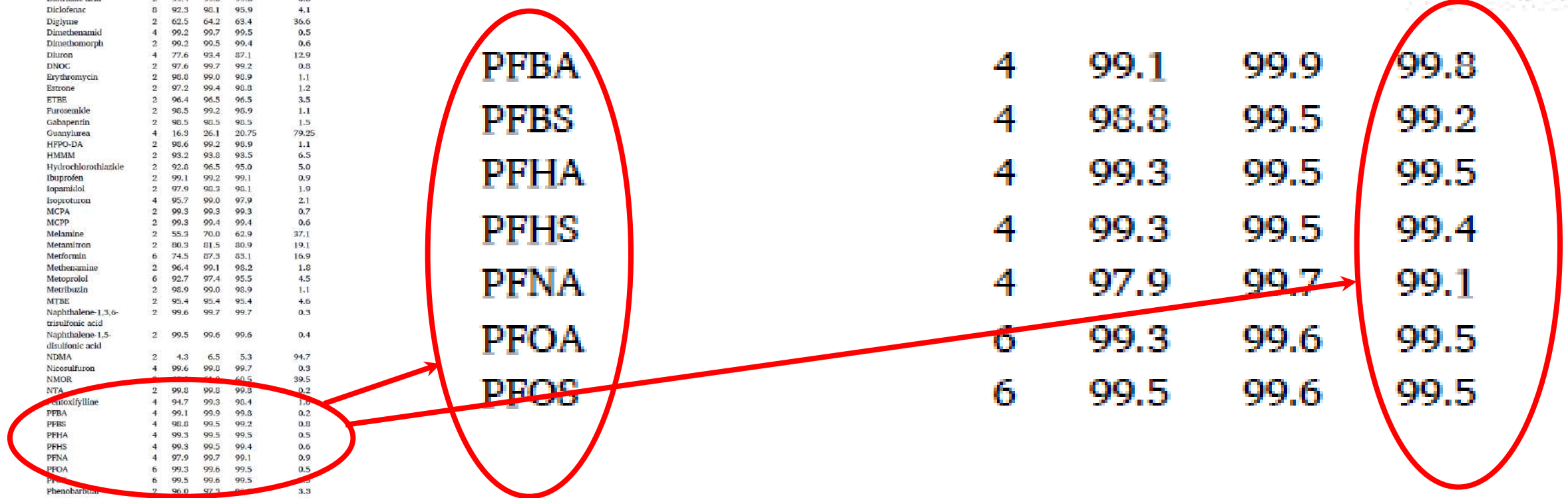
PFOA

6

99.5

99.6

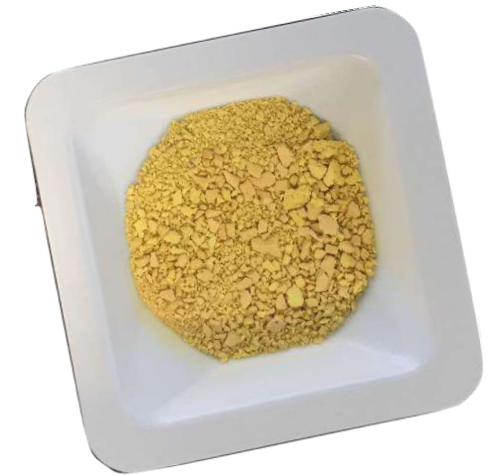
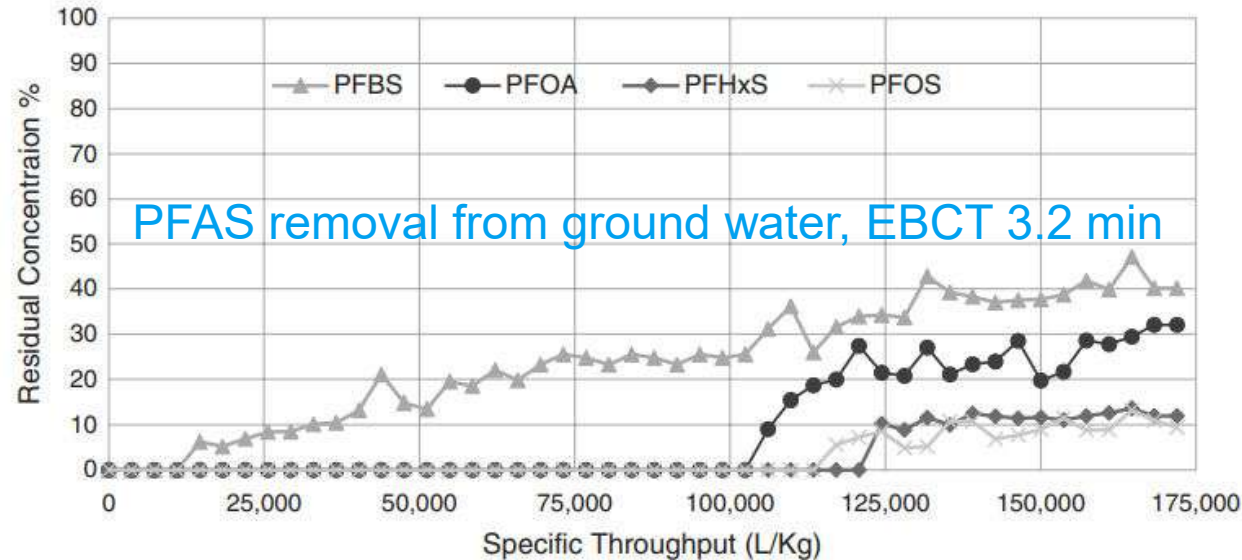
99.5



Future developments

- Cyclodextrine (glucose based) as alternative adsorbant:

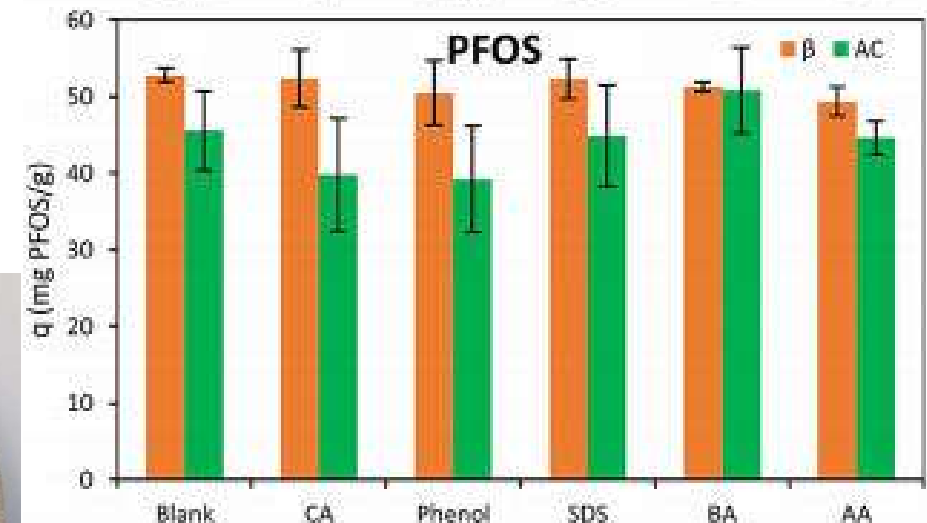
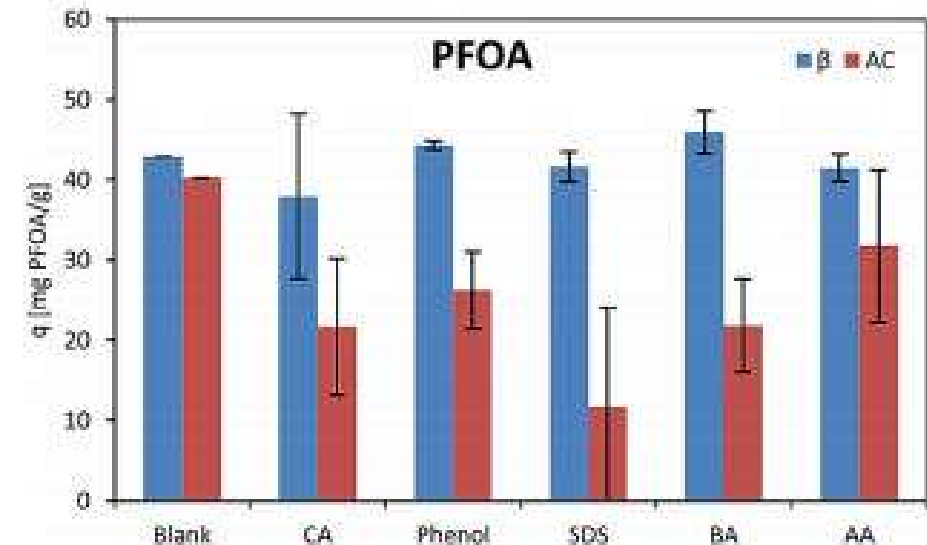
Wang et al., *ES&T Letters* 7(12) (2020), 954-960



- Costs? Sustainability?
- Application as pellets: abrasion?
- Regeneration (with methanol), residual waste?

Future developments

- All-Silica β -Zeolite as alternative adsorbent:
- Only PFOA and PFOS?
- Application in practice: granules?
- Regeneration?
- Costs? Sustainability?



Adsorption of PFOA and PFAS by β -Zeolite and AC in the presence of competing compounds

Conclusions

- Many CECs are present in the water cycle
- Many CECs introduce environmental risks and public health risks
- Resource protection is the way forward to protect drinking water quality
- Phasing out the use of persistent and mobile compounds protects the environment and guarantees a safe drinking water



Contaminants of Emerging Concern and Drinking Water Supply

jan.peter.van.der.hoek@waternet.nl

j.p.vanderhoek@tudelft.nl