

Reference situation PACAS RWZI Oijen

Waterboard Aa and
Meuse

Wim van der Hulst



content

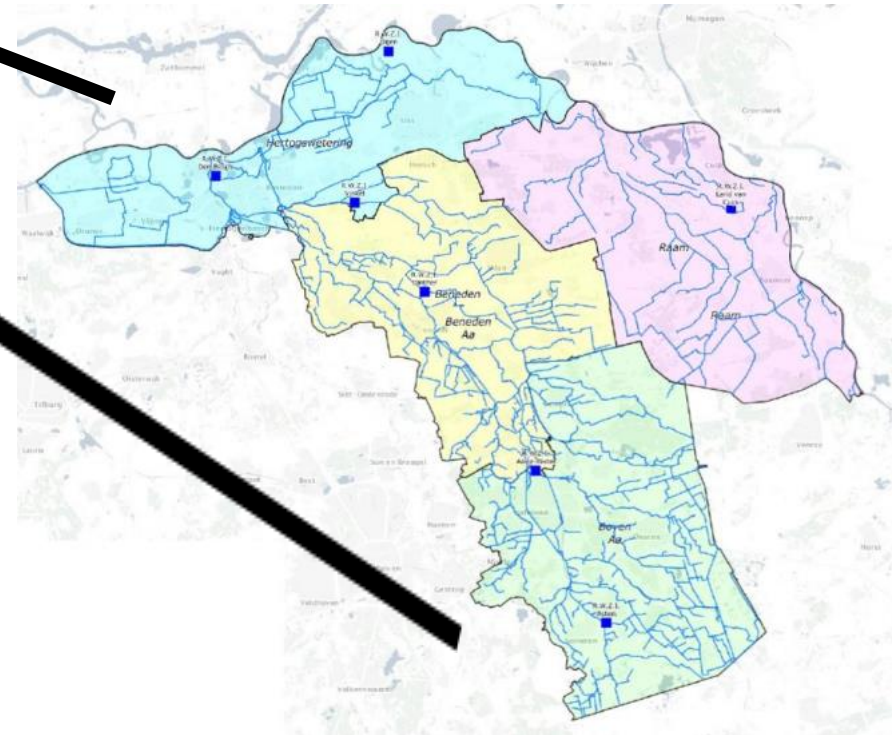
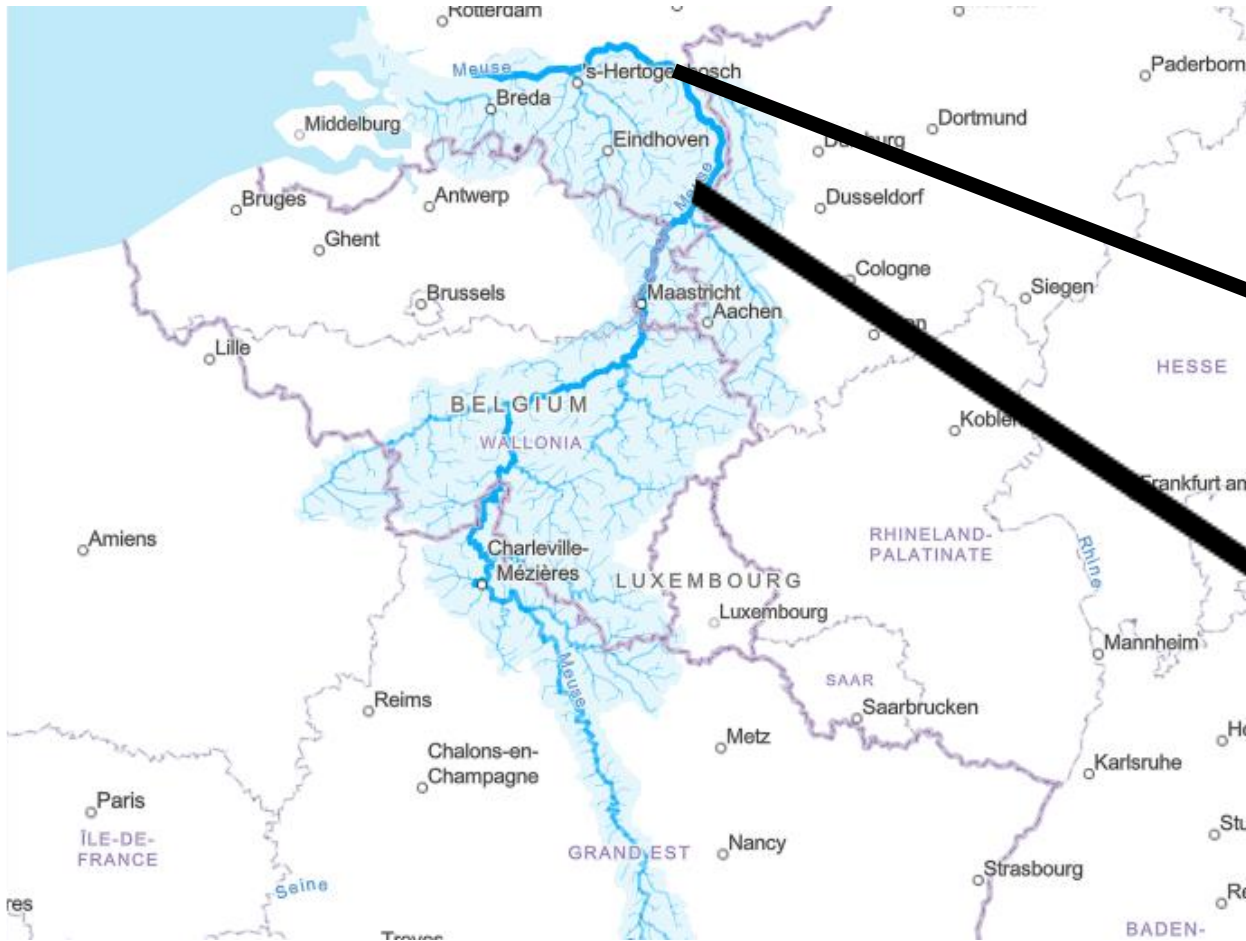
Introduction waterboard

Monitoring program

First results

Waterboard Aa en Maas

Elected administration
Own taxes
“Independent”



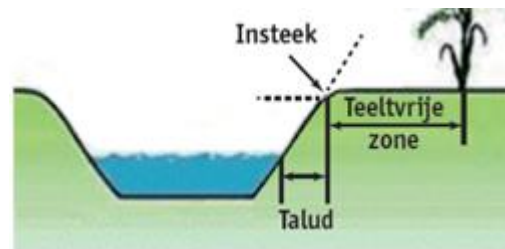


Dykes along the Meuse (*Meuse itself = Rijkswaterstaat*)

Enough surface- and groundwater
(preventing floods and droughts, maintenance)

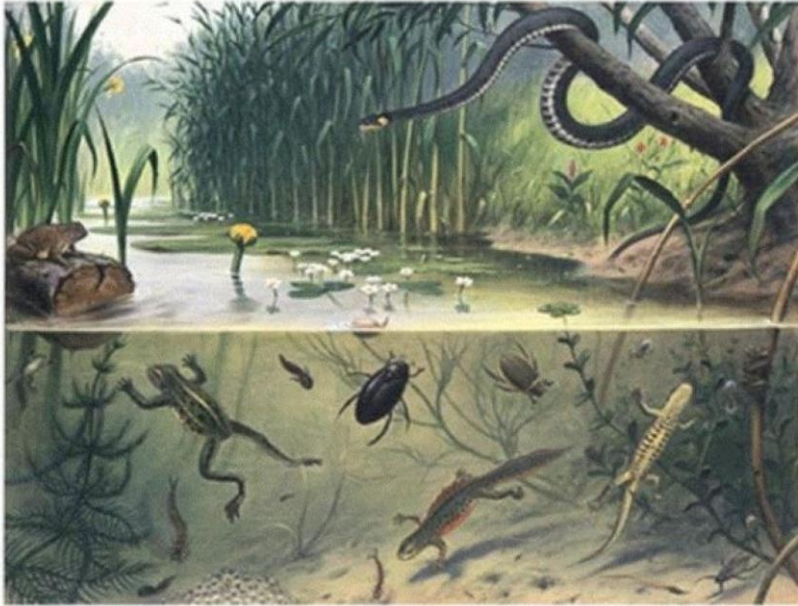
Surface water quality:

- Purification of wastewater 900.000 i.e.
- Monitoring quality and ecology (*WFD*)
- *Permits and surveillance (province or "gemeente" for wastewater in sewers)*



Goals waterquality

Water life

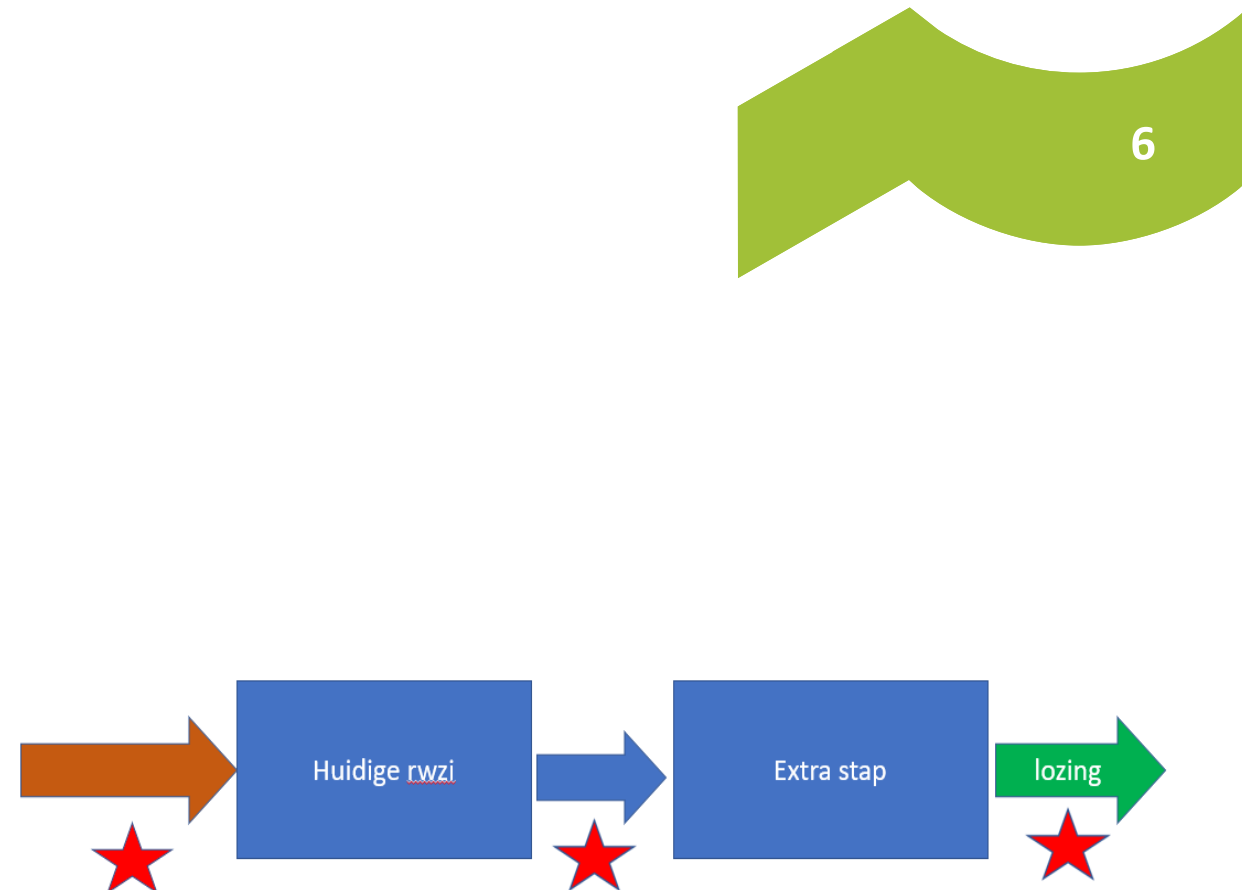


human use, like making drinkwater without having to use costly purification steps,



Situation 2020

- Database of measurements of organic pollutants, mostly plant protection substances. **Often above limits!**
- Should wtp's remove substances of concern from industry? Not the main solution
- Should WTP remove pharmaceuticals? Yes, the main way
- Financial contribution from ministry I&W (IPMV):
 1. 70% removal 7 of 11 gidsstoffen
 2. 50% reduction toxicity bioassays
- Why zero measurement?
 1. obligation IPMV;
 2. indication of necessity PACAS (*powdered activated carbon in activated sludge*),
 3. Effect PACAS on different substances.



What to measure?

- Earlier measurements
- WFD lists (policy), ZZS
- Drinking water
- Known to be used/ discarded
- “new” from screening
- “likely to be present because used” pharmaceuticals (RIVM)

Lab:
some substances are too expensive or hard to measure
Some substances are in a package with substances not asked to analyse

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	schone maaswat overwegige	maaswat overwegige	Groepsparamet	stof	CAS-numm	Pakket	gebruikt als													
215				sulpiride	15676-16-1	[Niet bekend]	genees													
216				tebuconazol	107534-96-3	3BESTR02 - G	fungicide													
217				telmisartan	144701-48-4	[Niet bekend]	genees													
218				temazepam	846-50-4	971LCTQ0x - i	genees													
219				terbutryn	886-50-0															
220				terbutylazine	5915-41-3	3BESTR02 - G	herbicide													
221 x				tetraglyme (tetraethyleenglycoldimethylether)	143-24-8	971KBSP401 -	koelmiddel, de-icing													
222 x?				tetrahydrofuraan (THF)	109-99-9	971KBSP401 -	oplosmiddel/polymeervormer													
223				Theophylline (xanthine of dimethylxanthine)	58-55-9		genees astma copd													
224				Thiofanaat-methyl	23564-05-8		gewasbescherming fungicide sinds 2021 verboden													
225				thiabendazol	148-79-8	903BRSCR01 -	schimmel, darmwormen													
226				thiacloprid (neonicotinoiden)	111988-49-9	3GEWAS02 -	gewasbescherming													
227				thiamethoxam (neonicotinoiden)	153719-23-4	903BRSCR01 -	Pakket GBM Brede screening													
228				tolclofos-methyl	57018-04-9	3BESTR02 - G	schimmel gewasbescherming													
229				tonalide	1506-02-1	971KBSP401 -	musk													
230				tramadol	27203-92-5	3HORGNMIO	genees pijnstillers, hoestonderdrukker													
231 x?				tri(2-chloorethyl)fosfaat	115-96-8	971KBSP301 -	KRW Brede screening perceel 3													
232				tributylfosfaat	126-73-8	971KBSP301 -	KRW Brede screening perceel 3													
233				trichloorazijnzuur	76-03-9	971HLHACOx	bijproduct chlooring, oplosmiddel													
234				trichloorpropylfosfaat	13674-84-5	971KBSP301 -	KRW Brede screening perceel 3													
235				triethylfosfaat	78-40-0	971KBSP301 -	brandvertragers													
236				trifenylfosfaat	115-86-6	971KBSP301 -	KRW Brede screening perceel 3													
237				trifenyfosfineoxide (TPPO)	791-28-6	971DEICIOx -	chemie ligand voor metalen													
238				trifluorazijnzuur	76-05-1	[Niet bekend]	bijproduct industrie													
239 x?				triglyme (Tri-ethyleenglycoldimethylether)	CAS 112-49-2		koelmiddel, de-icing													
240				triisobutylfosfaat	126-71-6	971KBSP301 -	KRW Brede screening perceel 3													
241				trimethoprim	738-70-5	3HORGNMIO	genees													
242				trimethylfosfaat	512-56-1	971KBSP301 -	KRW Brede screening perceel 3													
243 x?				tris(2-butoxyethyl)fosfaat	78-51-3	971KBSP301 -	brandvertragers													
244 x?				tris(2-ethylhexyl)fosfaat	78-42-2	971KBSP301 -	brandvertragers													
245				trisulfuron-methyl	126535-15-7	3GEWAS02 -	herbicide													

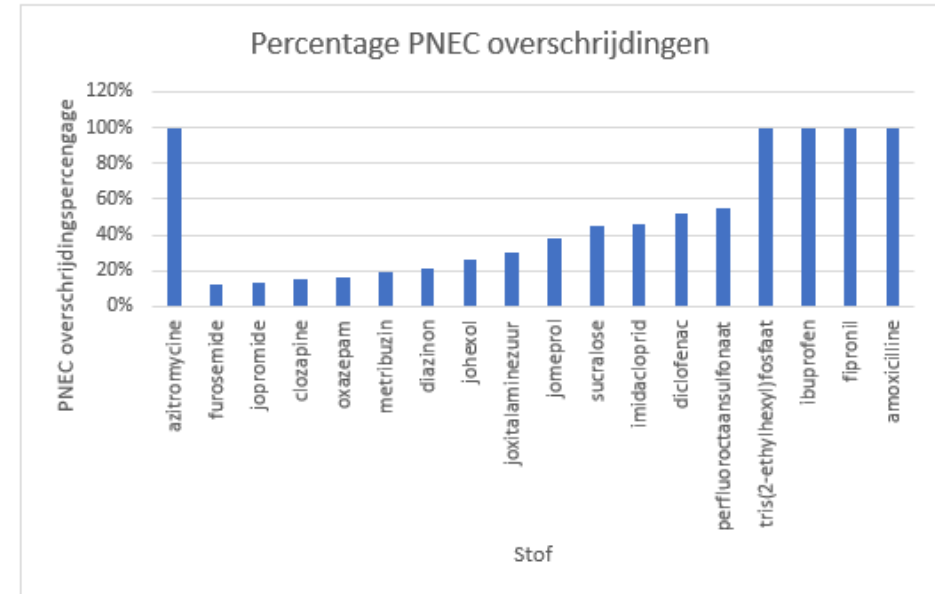
Measuring reference situation PACAS Oijen

- 374 substances
- Medicins, röntgencontrast, plant protection and biocides, PFAS-stoffen, hormones, sweeteners, organofosfaten, ftalaten, complexers like EDTA, industrial ZZS (*substances very high concern*), metals,
- Total 374 substances
- 6 measuring points (4 surface waters)
- Infl, effl and “HW beneden” more samples and substances
- November 2020 - december 2022
- Suspect screening
- biotests



Results in surface water and/or effluent wttp (at least found in 10% samples)

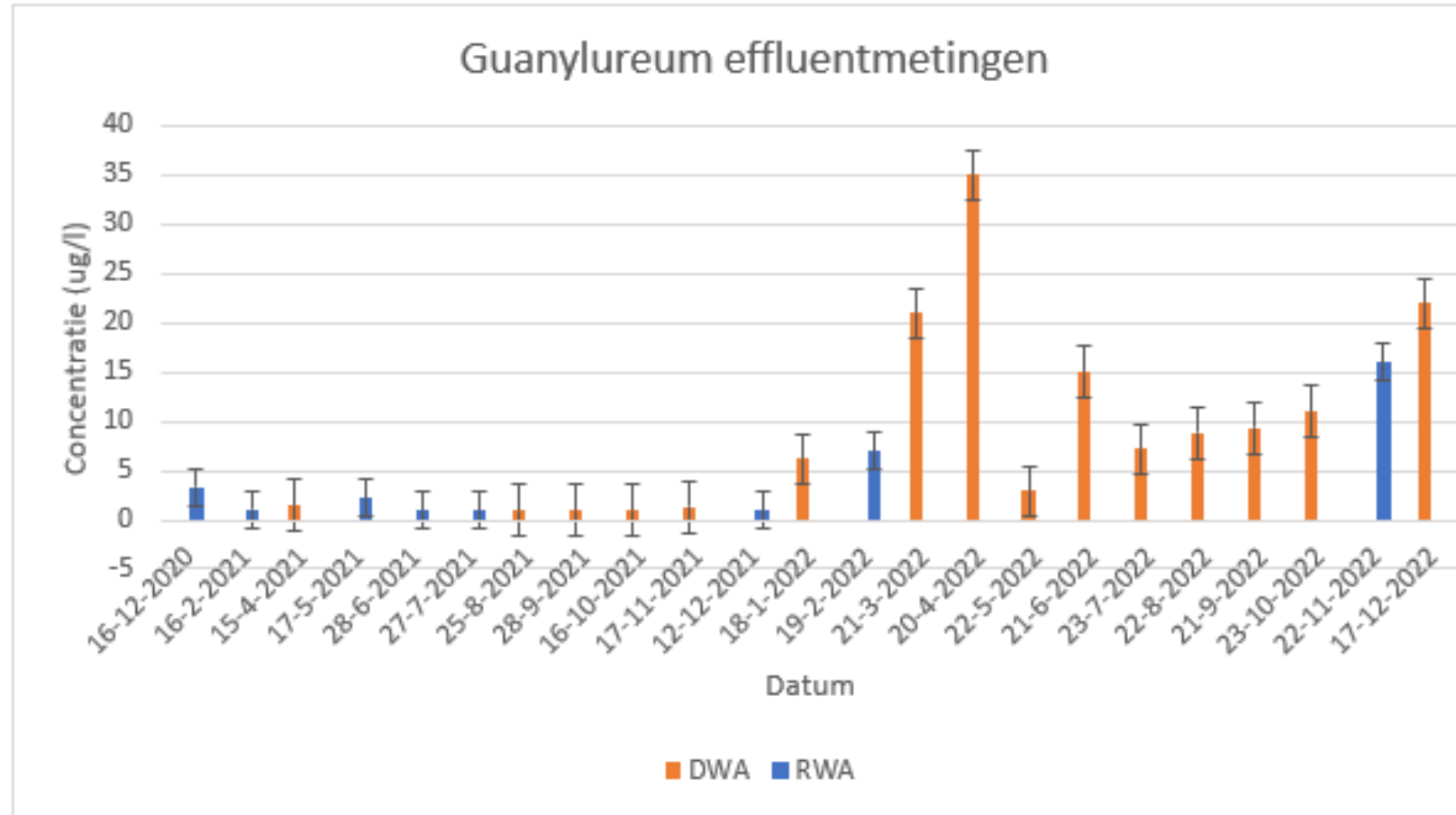
- **PNEC:** fipronil, azitromycine, diazinon, imadiclopid, diclofenac, furosemide, ibuprofen, perfluorooctaansulfonaat, johexol, jomeprol, jopromide, joxitalaminezuur
- **JG-MKN/P-JG-MKN:** diethyltoluamide, diazinon, imidaclopid, perfluorooctaansulfaat
- **MAC-MKN/P-MAC-MKN:** fipronil, azitromycine
- **DBS/P-DBS:** sucralose, benzotriazool, acesulfame K, AMPA, diethyltoluamide, difenoconazool, dimethomorf, EDTA, gabapentine, guanylureum, hydrochloorthiazide, irbesartan, metformine, methyl-1H-benzotriazool, metolachloor, metoprolol, natriumcyclamaat, oxypurinol, prosulfocarb, ritalinezuur, saccharine, som 4- en 5-methyl-1H-benzotriazool, tris(2-butoxyethyl)fosfaat, valsartan, glyfosaat



Concentrations

Large variations between samples

- dilution in sewer and surface water (rain or dry weather)
- Precipitation
- Formation metabolite
- Temperature
- Sampling strategy grab sample or 48/24 hour

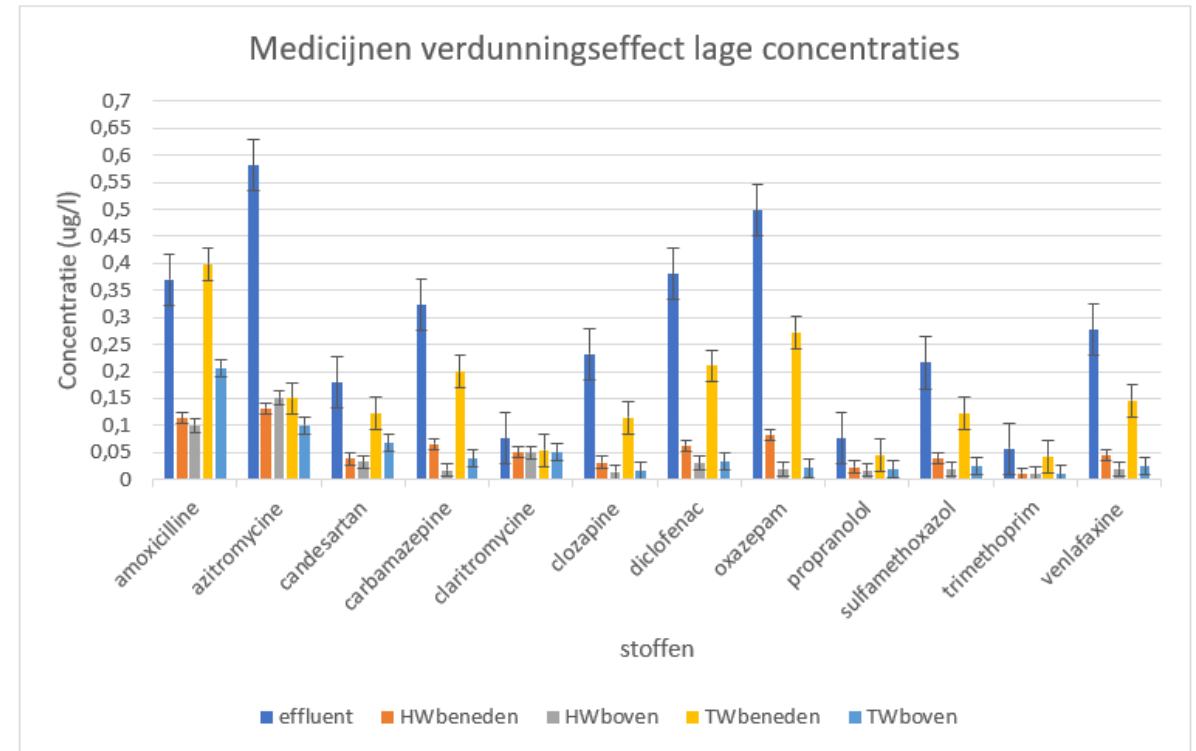


Guanylureum is metabolite of metformine (sugar disease)

dilution



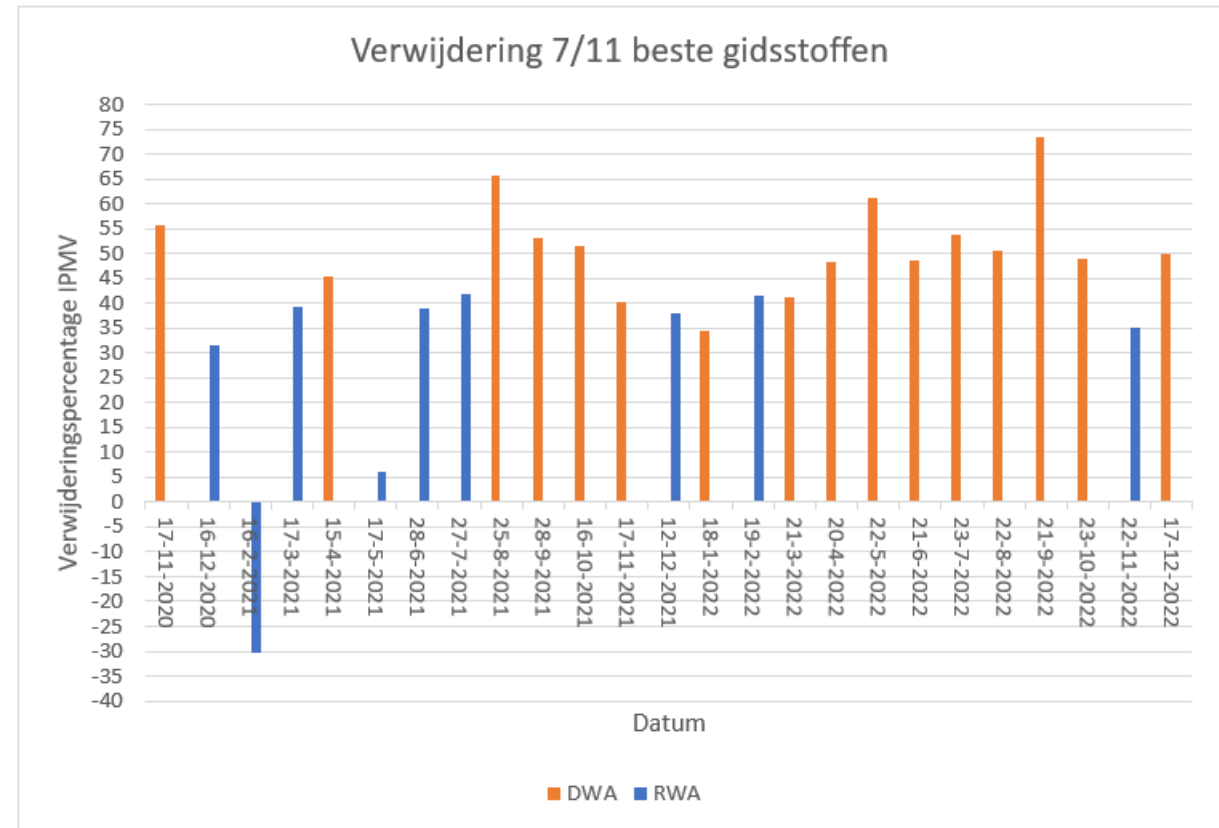
- Expected degradation concentrations -> effluent -> TWbeneden -> HWbeneden -> TWboven en HWboven
- Teeffelense wetering 50% effluent
- Hertogswetering benedenstrooms 25% effluent
- Lower concentrations of some substances present in Meuse water, that is pumped into our local water



Removal rate (pre-PACAS)



- Rule: 7/11 best gidsstoffen at least 70 procent removal
- Why is there removal?
 - Adsorption to sludge;
 - Biological degradation.



msPAF – how to classify?



- msPAF = meer stoffen Potentieel Aangetaste Fractie
- Of each substance measured concentration and toxicity
- WFD classification:
 - **geel** give attention, chronic effects max. 1/2 species
 - **Oranje** and **red** -> acute toxicity.

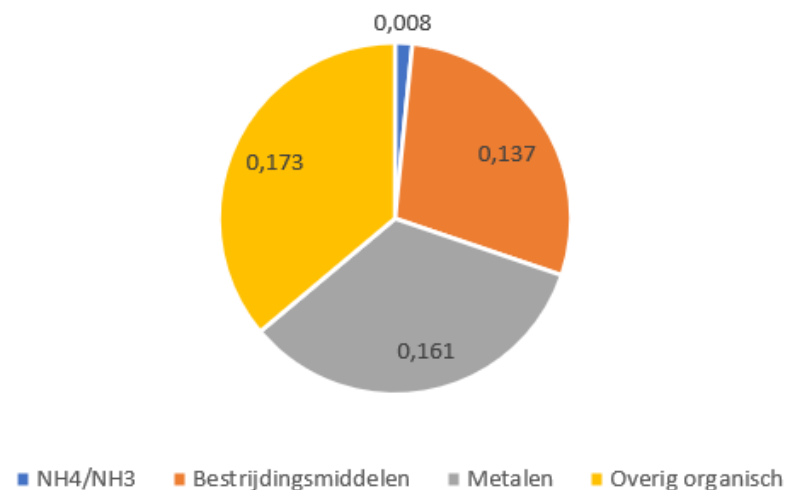
	KRW-bescherming		KRW-herstel		
Ecologische toestand	Zeer goed	Goed	Matig	Ontoereikend	Slecht
Ecotoxicologische toestand	Niet belast	Gering belast	Matige toxiciteit	Verhoogde toxiciteit	Hoge toxiciteit
Technische grenswaarde indien SSD beschikbaar was	ebmPAF 0.00 - 0.025	ebmPAF 0.025-0.05	ebmPAF 0.05-0.25	ebmPAF 0.25-0.50	ebmPAF 0.50-1.00
Technische grenswaarde indien SSD <u>niet</u> beschikbaar was	<0.1x ESW	0.1x ESW – ESW	≥ESW – 10x ESW	10x ESW – 100x ESW	>100x ESW
Woordelijke grenswaarde indien SSD beschikbaar was	Begin van hinder bij maximaal 1 op 20 soorten	Begin van hinder bij maximaal 1 op 4 soorten	Begin van hinder bij maximaal 1 op 2 soorten	Acuut toxisch	Acuut toxisch

Score msPAF



1
4

Gemiddelde effluent msPAF verdeling



No measurements of pH, T or hardness
So underestimation tox ammonium and metals?

Datum	Locatie	Totaal	NH4/NH3	Bestrijdingsmiddelen	Metalen	Overig organisch	n
17-11-2020	effluent	0,432	0,002	0,323	0,159		43
16-12-2020	effluent	0,179				0,179	28
16-2-2021	effluent	0,290	0,036	0,045	0,100	0,143	24
17-3-2021	effluent	0,284		0,025	0,111	0,174	27
15-4-2021	effluent	0,410	0,005		0,168	0,288	21
17-5-2021	effluent	0,424	0,013	0,269	0,054	0,156	20
28-6-2021	effluent	0,623	0,018	0,497	0,102	0,149	18
27-7-2021	effluent	0,505	0,002	0,092	0,128	0,374	30
25-8-2021	effluent	0,305	0,001	0,111	0,109	0,121	22
28-9-2021	effluent	0,332	0,015	0,031	0,147	0,179	28
16-10-2021	effluent	0,768	0,007	0,663	0,217	0,115	23
17-11-2021	effluent	0,490	0,003		0,202	0,359	31
12-12-2021	effluent	0,488	0,008		0,360	0,194	21
18-1-2022	effluent	0,377	0,001	0,057	0,236	0,135	33
19-2-2022	effluent	0,417	0,015	0,095	0,248	0,131	16
21-3-2022	effluent	0,384	0,001	0,099	0,160	0,186	27
20-4-2022	effluent	0,344	0,001	0,040	0,142	0,203	17
22-5-2022	effluent	0,242	0,005	0,046	0,107	0,107	32
21-6-2022	effluent	0,233	0,001	0,007	0,106	0,136	18
23-7-2022	effluent	0,418	0,004	0,031	0,212	0,235	16
22-8-2022	effluent	0,196	0,001	0,074	0,040	0,094	10
21-9-2022	effluent	0,297	0,003	0,079	0,159	0,090	19
23-10-2022	effluent	0,307	0,008		0,209	0,117	18
22-11-2022	effluent	0,402	0,019	0,153	0,164	0,139	17
17-12-2022	effluent	0,327	0,006	0,000	0,219	0,133	25

Bioassays

- Bioassay = biologische effectmeting (op cels/species)
- Not all tests give an affect;
- *Effl en teef.w beneden oranje.*
Orange -> action
- *Hw beneden yellow => tox is limited, less urgent.*

Locatie	GR CALUX	Era CALUX	PAH CALUX	PXR CALUX	Microtox	Daphniatox
Gemiddelde effluent	34,10	15,72	193,73	35,89	0,04	0,02
Gemiddelde twbeneden	19,60	5,24	211,67	20,59	0,03	0,02
Gemiddelde hwbeneden	3,78	1,69	42,70	12,24	0,02	0,02
Gemiddelde twboven	4,24	0,90	59,04	9,24	0,02	0,02
Gemiddelde hwboven	1,17	0,09	40,56	3,64	0,02	0,02
Gemiddelde blanco	12,46	1,32	133,48	13,42	0,02	0,02

Comparison msPAF and effect tests

- msPAF versus bioassay
- ESW = Effect Signaal Waarde

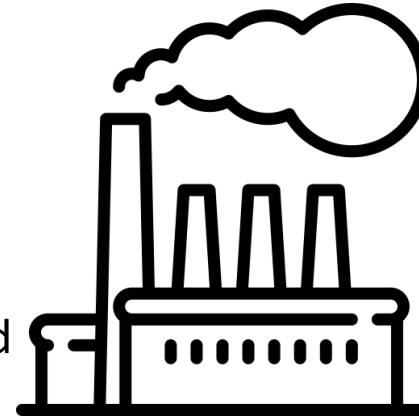
Column esw differs from next two columns.

- ESW inaccurate?
- ESW is triggered by other substances than measured (and used in mspaf)

Effluent	Gemiddelde aantal x ESW	msPAF compleet (chronisch)	msPAF shortlist (chronisch)
nov-20	7,341558891	0,432	0,191
dec-20	14,21901855	0,179	0,179
jun-21	1,099021415	0,623	0,561
jul-21	7,982727747	0,505	0,431
aug-21	4,627624557	0,305	0,219
sep-21	9,518313029	0,332	0,205
okt-21	12,58700664	0,768	0,701
nov-21	8,763028797	0,49	0,35
dec-21	10,09338336	0,488	0,194
jan-22	19,67420633	0,377	0,183
feb-22	4,81216117	0,417	0,213
mrt-22	7,167530957	0,384	0,265
apr-22	7,863026462	0,344	0,234
mei-22	4,711824891	0,242	0,146
jun-22	6,104487596	0,233	0,14
jul-22	6,24566083	0,418	0,257
aug-22	7,757877423	0,196	0,161
sep-22	7,862099437	0,297	0,105
okt-22	5,863334793	0,307	0,117
nov-22	13,09456869	0,402	0,188

Conclusions

- All kind of substances present in concentrations above environmental limits / limits for making drinkwater
- Only minority pharmaceuticals, rest Biocides, pesticides, Substances of Very High Concern (in Dutch: Zeer Zorgwekkende Stoffen)
- This makes PACAS usefull, but also better regulation industry, REACH, SVHC, substances used in households,
- **High** toxicity in effluent, **lower** when diluted (local problem AND action on several wttp needed for problems
- Combination of measuring effluent and surface water usefull
- Combination of measuring substances and calculation tox and bioassays usefull



Questions?