D4RUNOFF

Recognising CECs even when they are hidden

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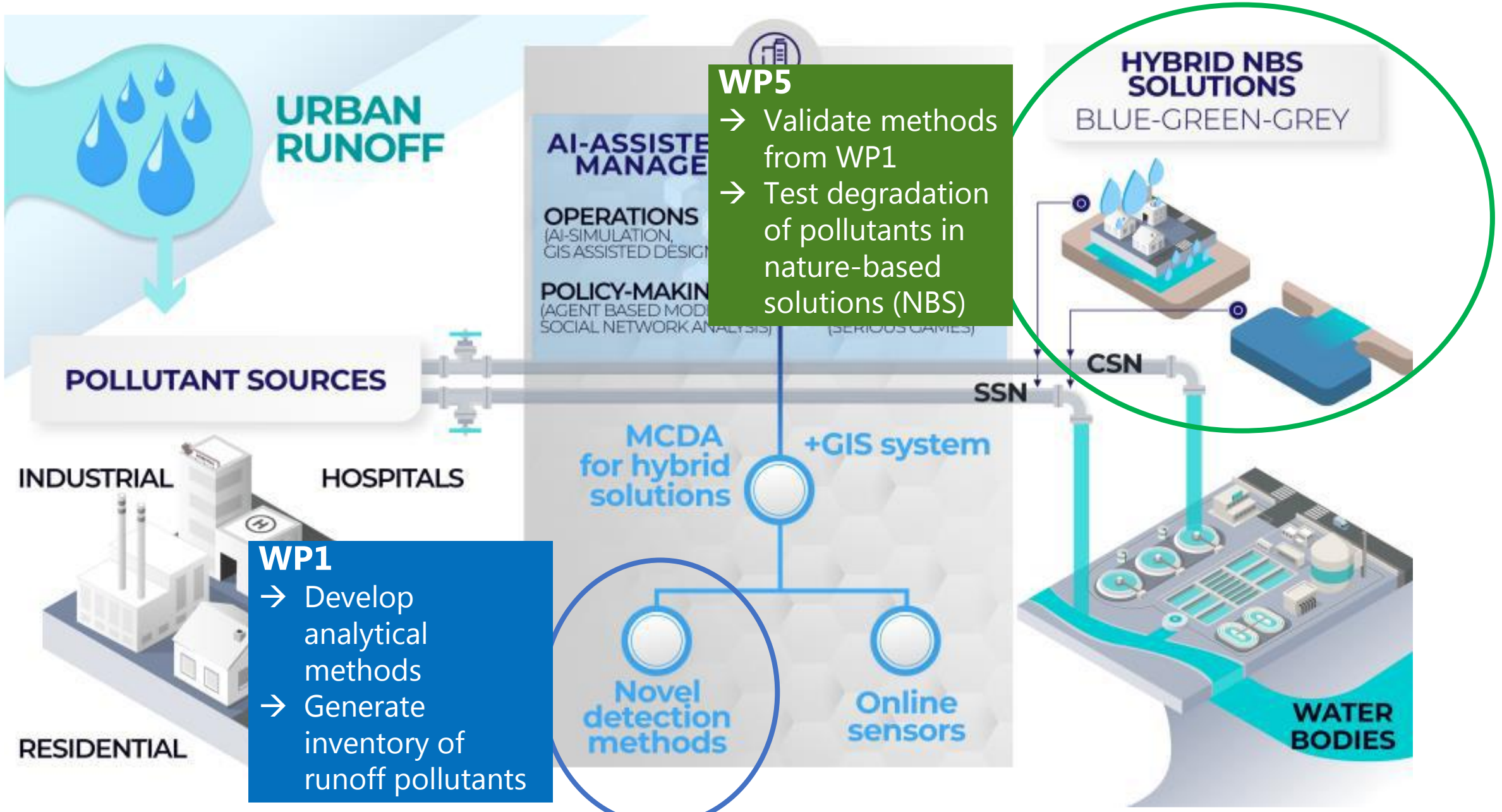


WP5

- → Validate methods from WP1
- → Test degradation of pollutants in nature-based solutions (NBS)

WP1

- → Develop analytical methods
- → Generate inventory of runoff pollutants

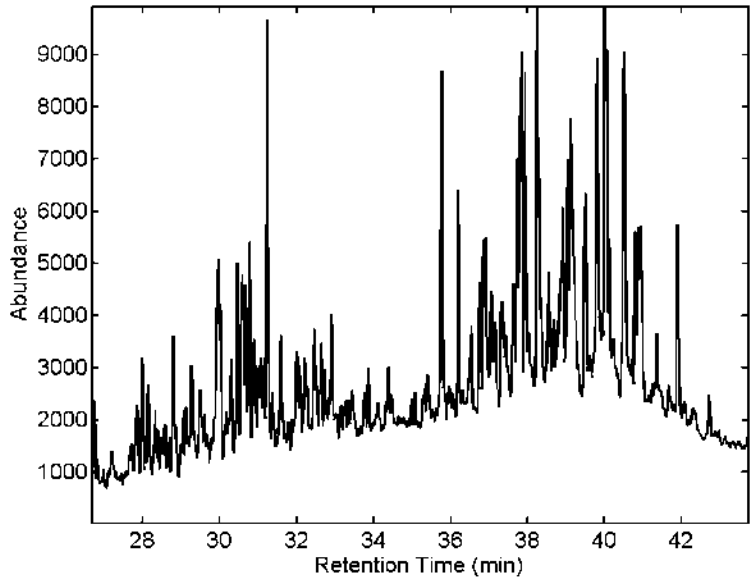
What is a chemical fingerprint?

Human Fingerprint

- Impression of the underside of the end of a finger, used for identification
- The arrangement of ridges is thought to be **unique** and **permanent** with each person
- No two persons with the same prints have ever been found

Chemical fingerprint

- A **unique** chemical pattern
- Used to determine the identity of emerging contaminants, mixture of pollution sources, effects of bioremediation initiatives etc.
- Not necessarily **permanent**



Different types of chemical fingerprints

- ✓ Find all chemical substances in a sample?
- ✓ Identify the substances
- ✓ Determine the concentration

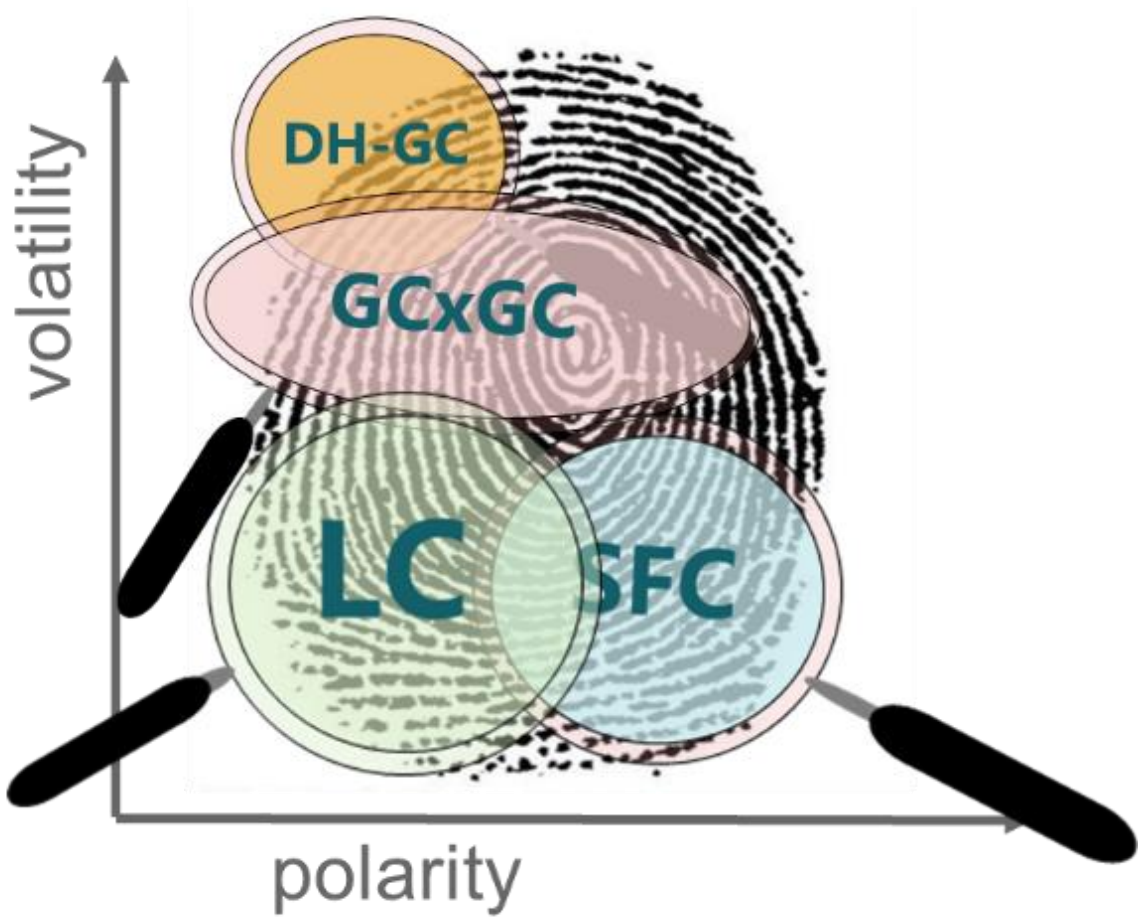
- ✓ Which substances pose a problem (persistent, toxic, concentrations)?
- ✓ What are their sources?
- ✓ How can they be removed most cost-effectively using nature-based solutions
- ✓ Or is it better to let them enter the wastewater treatment plants?

Extremely high focus on concentrations and limit values of a small number of chemical substances

Target analysis	Suspect screening	Non-target screening (NTS)
$	$	$
$	$	$
$	$	$
$	$	$
$	$	$

Target, suspect, and non-target screening analysis

There is not one “fingerprint” to rule them all



You only find what you look for

6PPD-Quinone

Salmon have been dying mysteriously on the West Coast for years. Scientists think a chemical in tires may be responsible

By Drew Kann, CNN
4 minute read · Published 4:11 PM EST, Thu December 3, 2020

A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon

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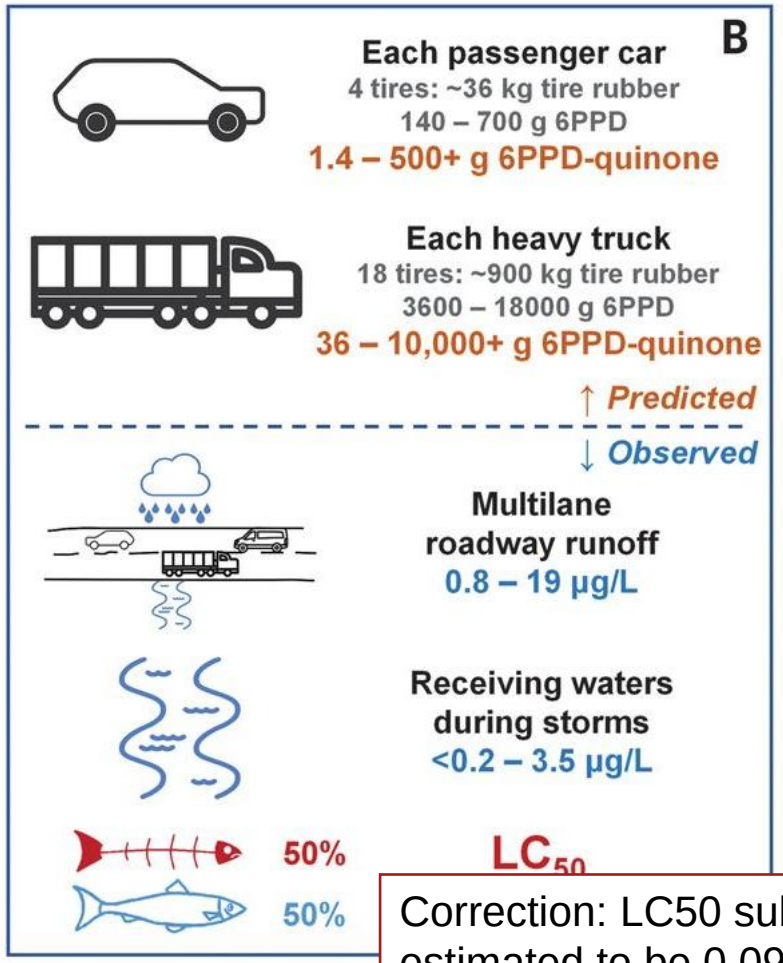
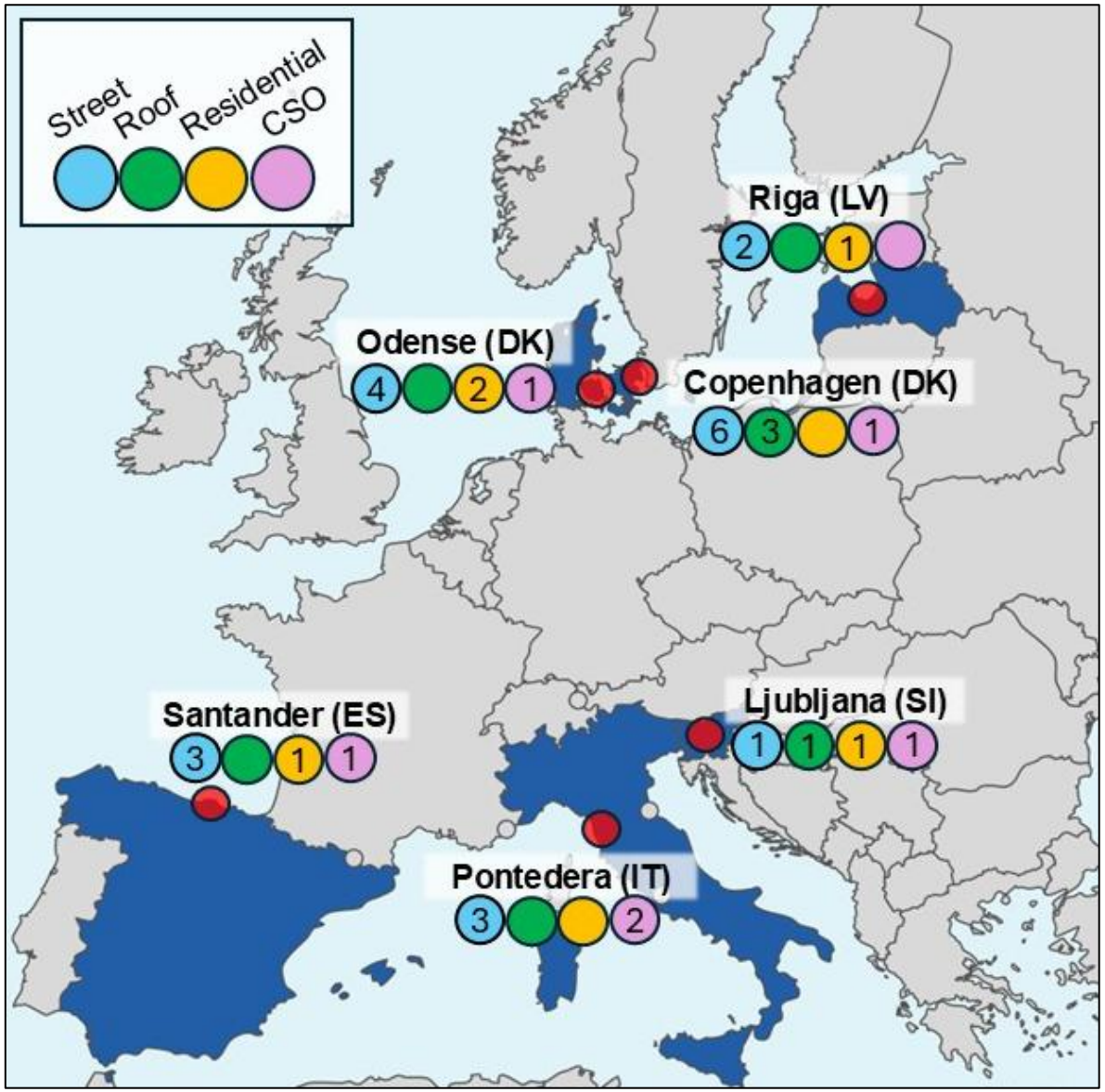


Correction: LC50 subsequently estimated to be 0.095 µg/L

What we did in D4RUNOFF

WP1 samples

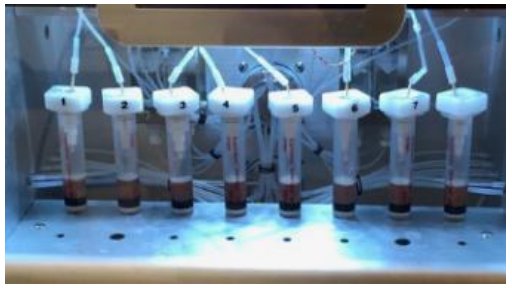
- 34 runoff samples from around Europe covering different catchment areas
- Sampling over two hours from start of rain event



Sampling and sample preparation

Sampling

Filtration



Liquid fraction

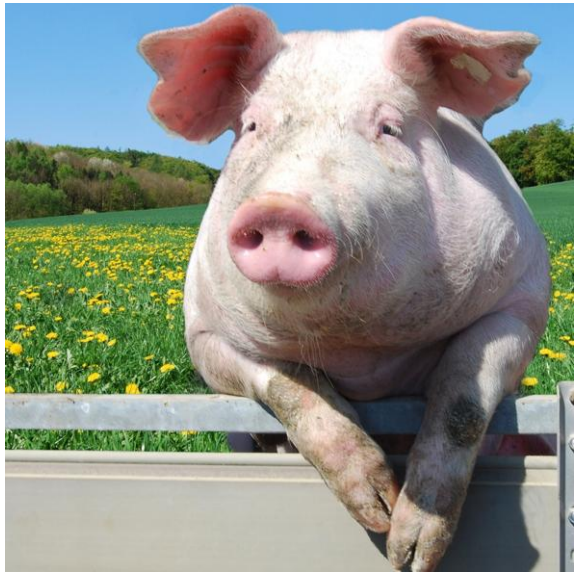
SPE

Dissolved pollutants

LC-HRMS
HILIC-HRMS
GC×GC-HRMS

Sorbed pollutants + microplastics

Py-GC-MS
GC×GC-HRMS



[So what]

Danish phonetics

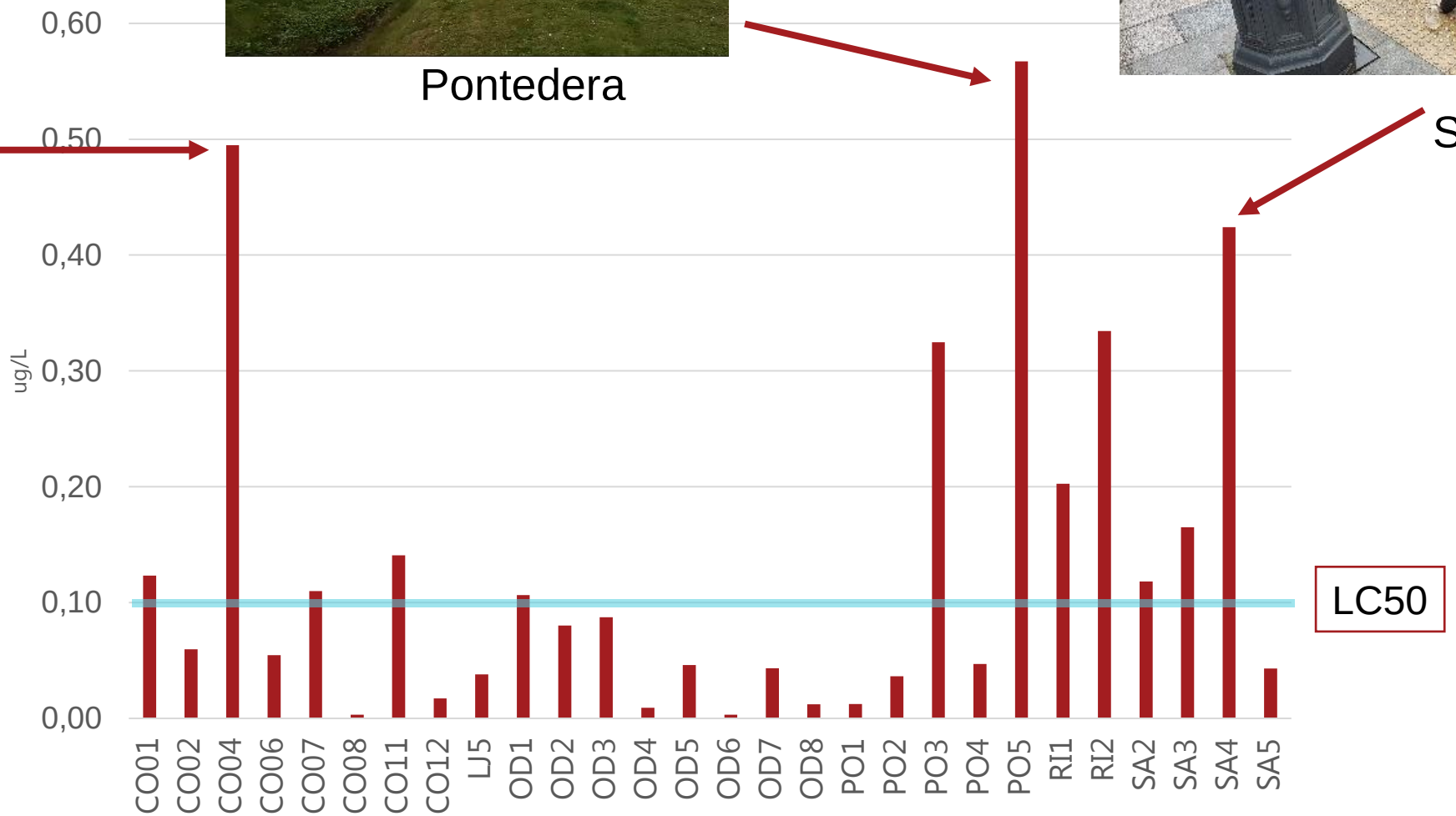
...Have we found?

6PPD-quinone

Copenhagen
Rolighedsvej

Pontedera

Santander



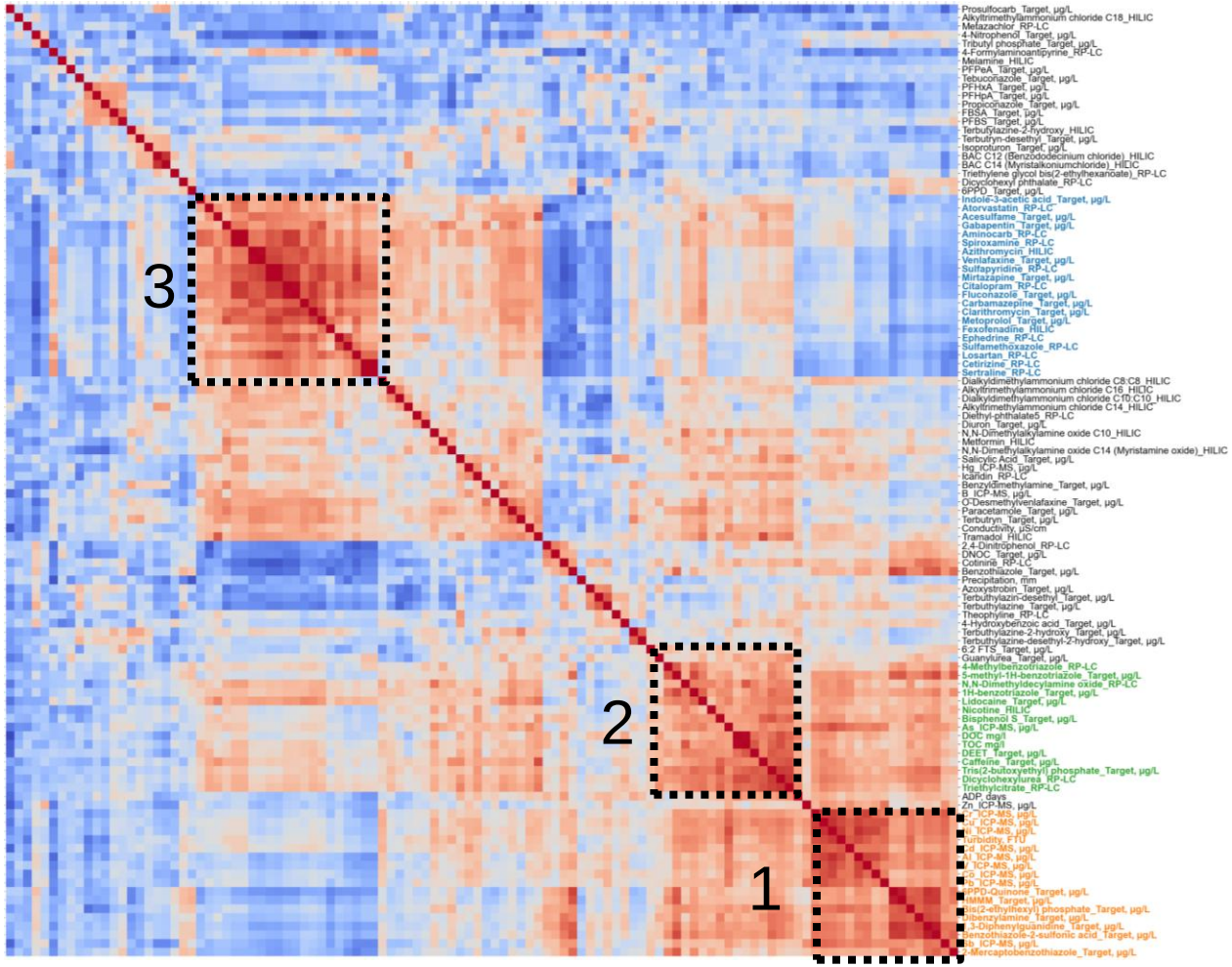
Pollution sources (target and suspect screening)

Three largest clusters of correlating compounds

Cluster 3 CSO
- Pharmaceuticals (citalopram, gabapentin, losartan...)
- Artificial sweetener (acesulfame)

Custer 2 ?
- Corrosion inhibitors (benzotriazoles)
- Caffeine
- Nicotine

Cluster 1 Street runoff
- Rubber compounds (6PPD-Q, HMMM, 1,3-diphenylguanidine...)
- Metals (Cu, Zn, Ni, Pb...)



LC-HRMS results (target and suspect screening)

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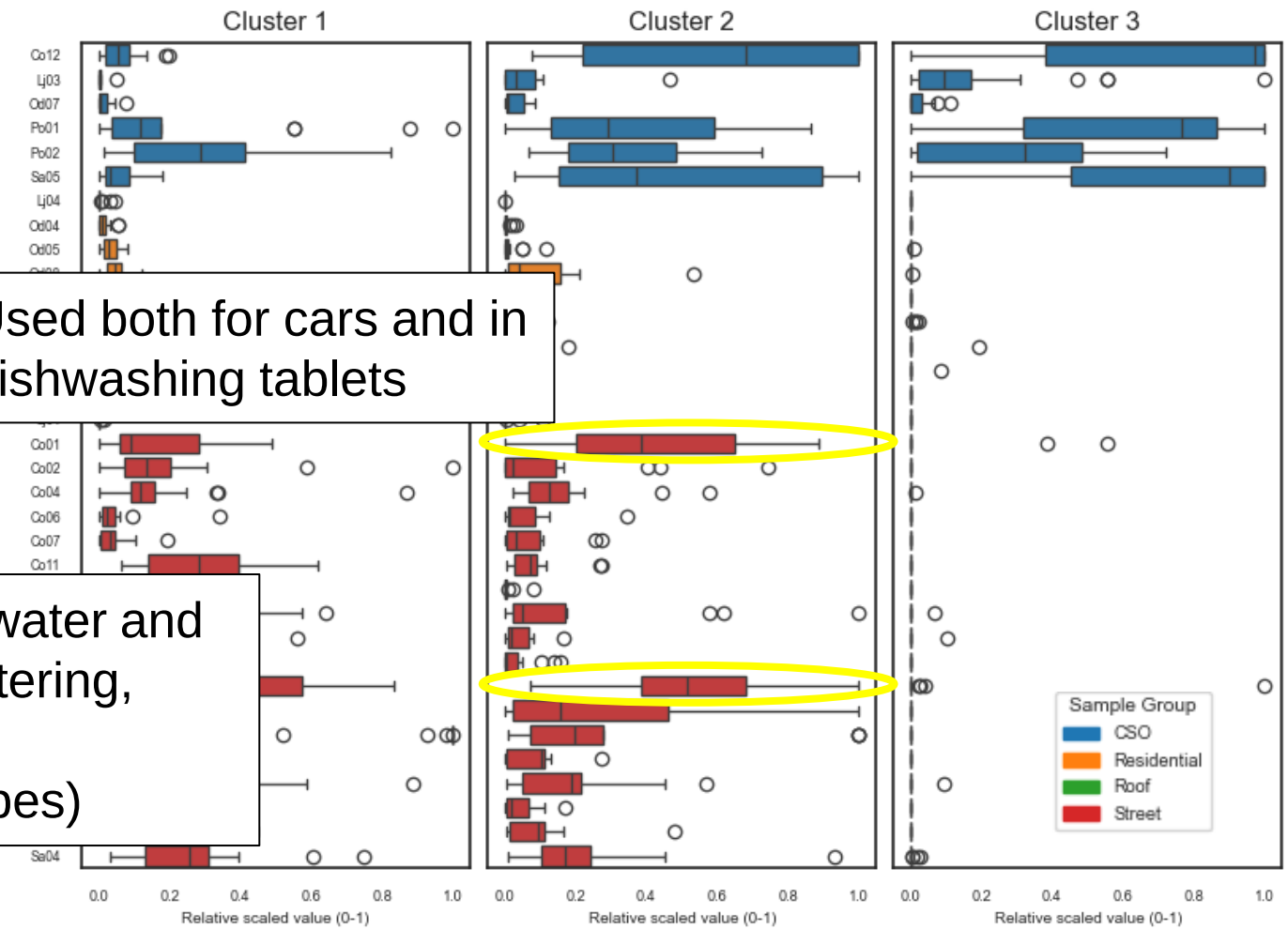
Cluster 1 Street ru
- Rubber compou
  HMMM, 1,3-diphenylguanidine...)
- Metals (Cu, Zn, Ni, Pb...)

Used both for cars and in dishwashing tablets

Both from wastewater and surface runoff (littering, public urination, misconnected pipes)



Unexpected pollution sources

Relative concentration (0-1)
Red = high relative concentration
Blue = low relative concentration
White = not detected

		CSO						Street	
		Co12	Lj03	Od07	Po01	Po02	Sa05	Co01	Po03
Acesulfame (Target)	Other	0.97	0.07	0.04	0.62	0.32	1.00	0.38	
Caffeine (Target)	Other	1.00		0.02	0.26	0.11	0.37	0.24	0.07
DNOC (Target)	Other		0.01	0.08		0.09	0.04	0.04	0.03
Cotinine (RP-LC)	Other							0.92	0.73
Triethylcitrate (RP-LC)	Other	1.00	0.09	0.08	0.86	0.54	1.00	0.66	0.48
Nicotine (HILIC)	Other	0.25		0.00	0.10	0.22	0.03	0.12	1.00
Carbamazepine (Target)	Pharmaceuticals	0.23	1.00		0.73	0.35	0.18		0.04
Clarithromycin (Target)	Pharmaceuticals	0.08	0.17		1.00	0.34	0.45		0.02
Fluconazole (Target)	Pharmaceuticals	0.38	0.10		1.00	0.44	0.30		
Gabapentin (Target)	Pharmaceuticals	0.18		0.01	0.10	0.04	0.14		1.00
Guanylurea (Target)	Pharmaceuticals	0.15	1.00				0.12	0.11	0.12
Lidocaine (Target)	Pharmaceuticals	1.00	0.47	0.01	0.78	0.18	0.52	0.21	0.32
Metoprolol (Target)	Pharmaceuticals	1.00	0.02	0.05	0.24	0.05	0.02		0.03
Mirtazapine (Target)	Pharmaceuticals	0.68	0.55	0.02	0.35	0.12	1.00		
O-Desmethylvenlafaxine (Target)	Pharmaceuticals	0.34	0.25	0.02	0.32	0.04	1.00	0.10	0.10
Paracetamole (Target)	Pharmaceuticals	1.00	0.00	0.03	0.11	0.06	0.89	0.04	0.00
Venlafaxine (Target)	Pharmaceuticals	0.88	0.47	0.03	0.32	0.08	1.00		
Azithromycin (HILIC)	Pharmaceuticals	0.67	0.55	0.00	1.00	0.72	0.68		
Fexofenadine (HILIC)	Pharmaceuticals	1.00	0.31	0.07	0.01	0.02			
Metformin (HILIC)	Pharmaceuticals	1.00				0.32	0.43		0.02
Tramadol (HILIC)	Pharmaceuticals	1.00	0.04	0.09	0.49	0.16	0.60	0.07	0.04
Atorvastatin (RP-LC)	Pharmaceuticals	1.00			0.70		0.83	0.55	

Hospital

PO03

Surface runoff with high concentration of individual pharmaceuticals (gabapentin, lidocaine..)

Nearby hospital → littering of pharmaceutical packaging?

CO01

Stormwater drain with high concentration of wastewater indicators (acesulfame, caffeine, paracetamole)

Inner city area → public urination and/or misconnected pipes?

Top 5 metals and organic pollutants

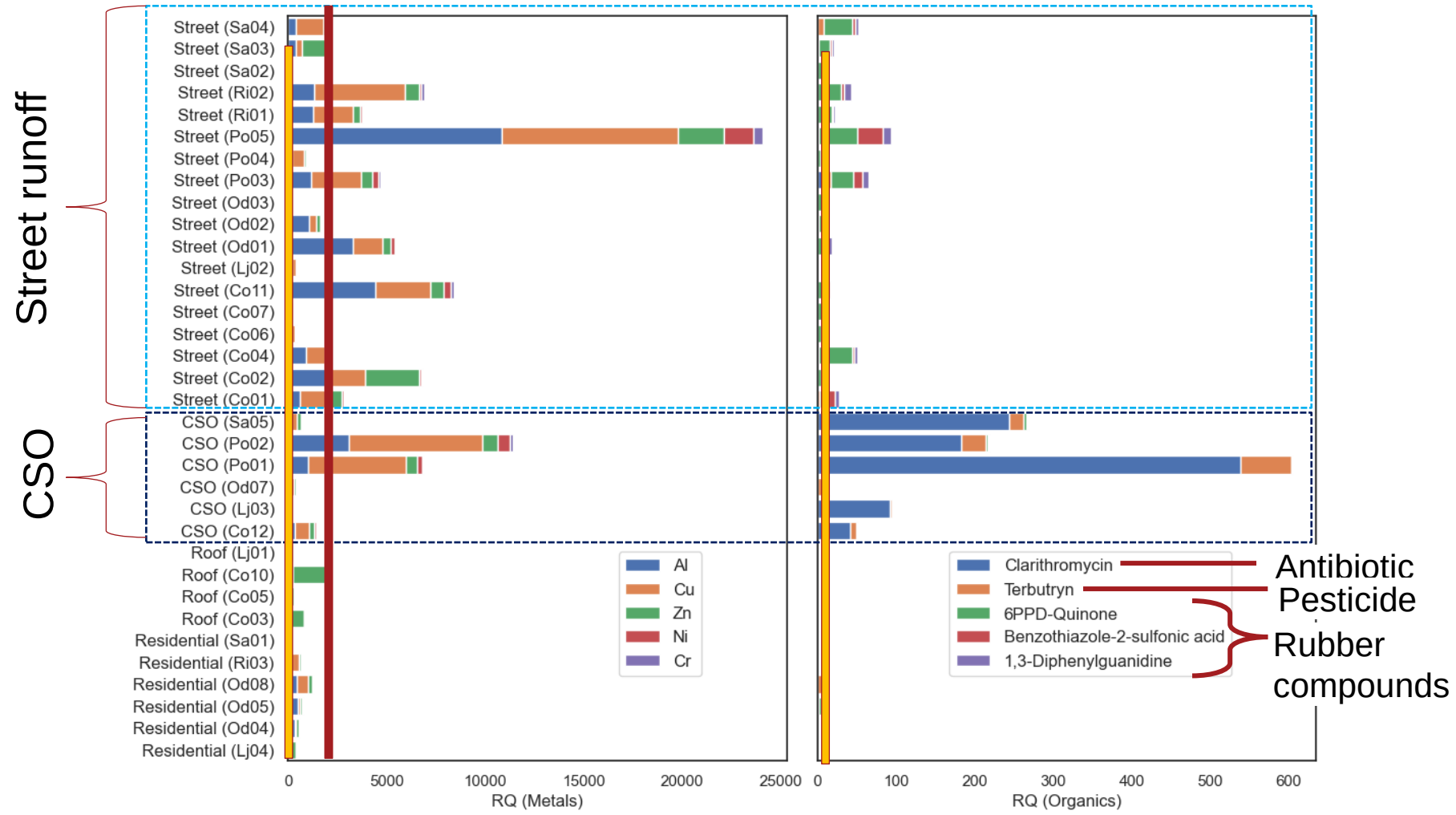
Risk quotient (RQ)
$= \frac{Measured\ concentration}{LC50/1000}$

RQ > 1
→ Measured concentration above PNEC

RQ > 1000
→ Measured concentration above LC50

Street runoff and CSO have highest RQ

BUT also other types of runoff have RQ > 1, especially from metals

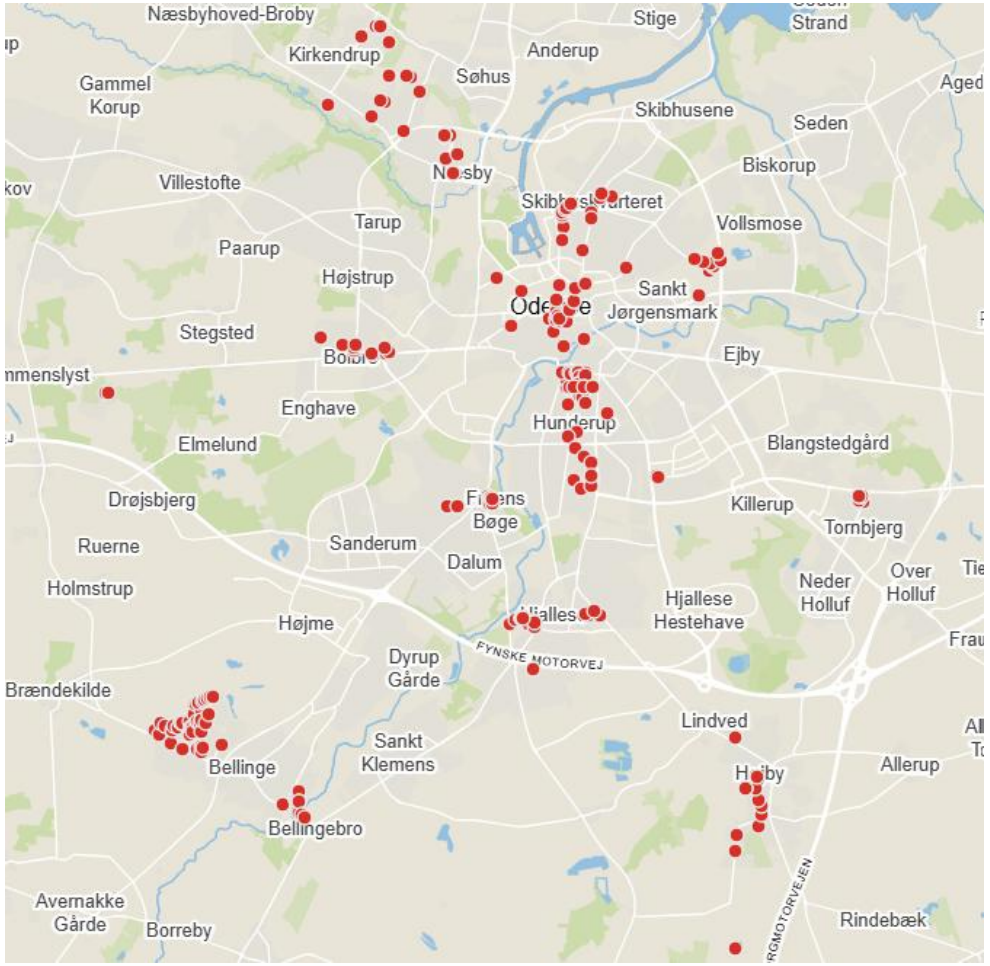


Max RQ of the included organisms (fish, daphnia, algae)

High-throughput: Citizen Science in Odense

- Simple sampling workflow
- Fast analytical method

→ 300 samples have been analysed



Acknowledgements

D4RUNOFF

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