Trends in de chemische analyses

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30 januari 2019

@KWR_Water

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Chemicals – which ones to measure?

Knowns

- Industrial compounds,
- pharmaceuticals,
- pesticides,
- artifical sweeteners, ect

Unknowns

- Transformation products
- Water treatment

New technologies:

- Nanoparticles
- Microplastics

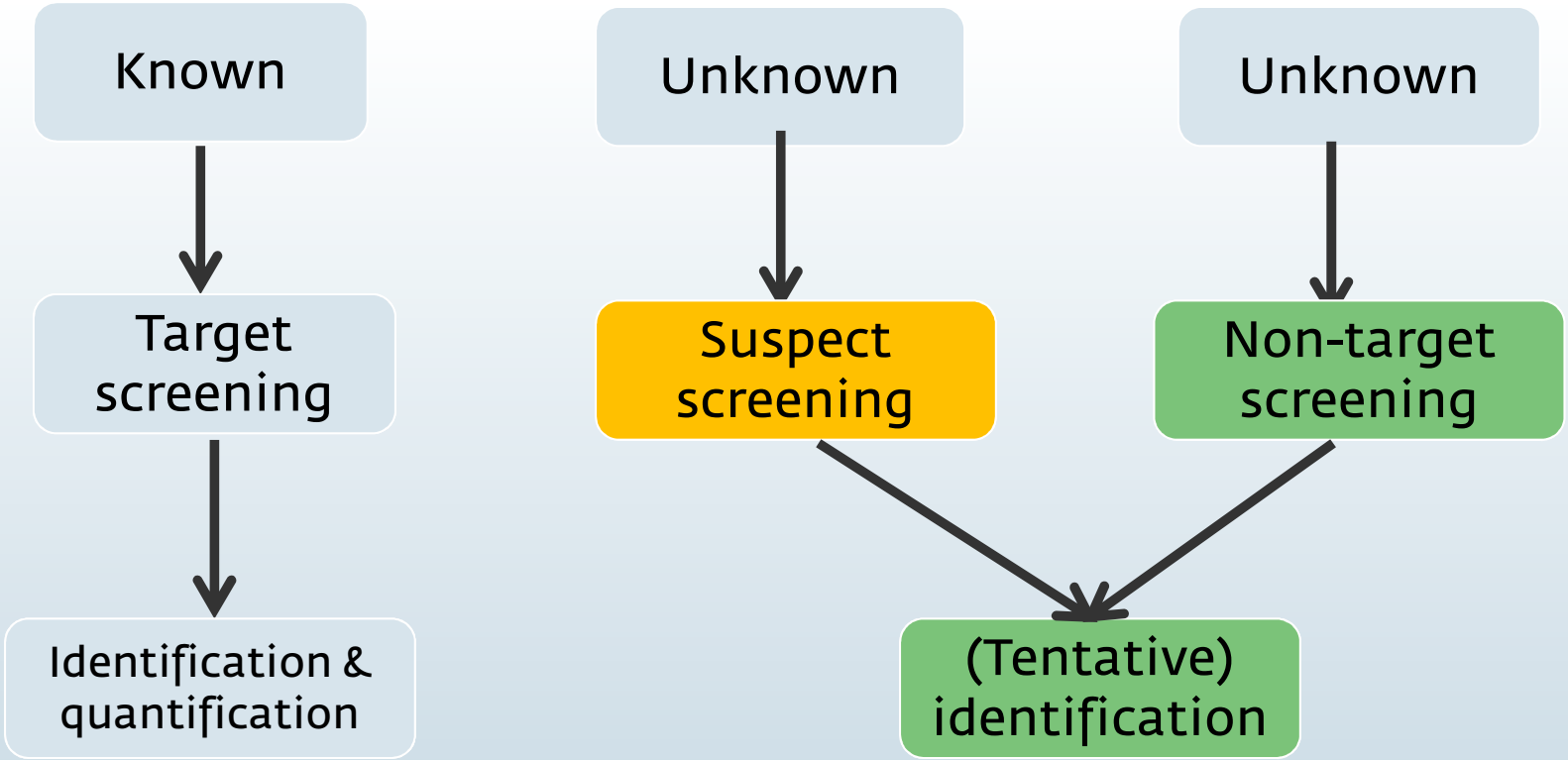
Trends

Chemische analyse van de waterkwaliteit

1. Suspect en Non-target screening
2. Zeer polaire stoffen
3. Bioassays
4. Analyse van deeltjes (nanoparticle, microplastics)

Trend 1

Target, suspect en non-target screening



Suspect Screening en Non Target Screening

Hoge resolutie massaspectrometer

Orbitrap Fusion - Thermo Scientific

QToF TripleTOF 5600+ Sciex

Non-target screening

Hoge resolutie, accurate massaspectrometrie

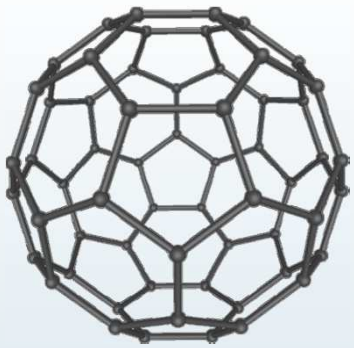
Not looking only at targets anymore

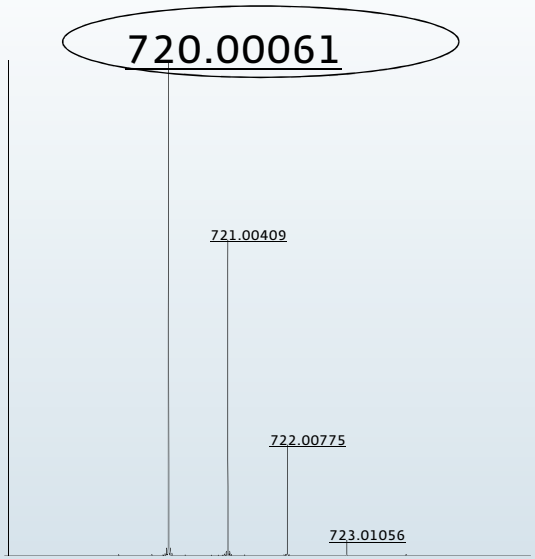
Buckyball "C_{60}"

Accurate mass: 60x 12 = 720

1 electron weegt 0.00055 amu

But,… $[M]^{1-}$ is measured





Hoge resolutie MS

Samenstelling/brutoformule vaststellen

Elementen

C = 12.00000 N = 14.00307

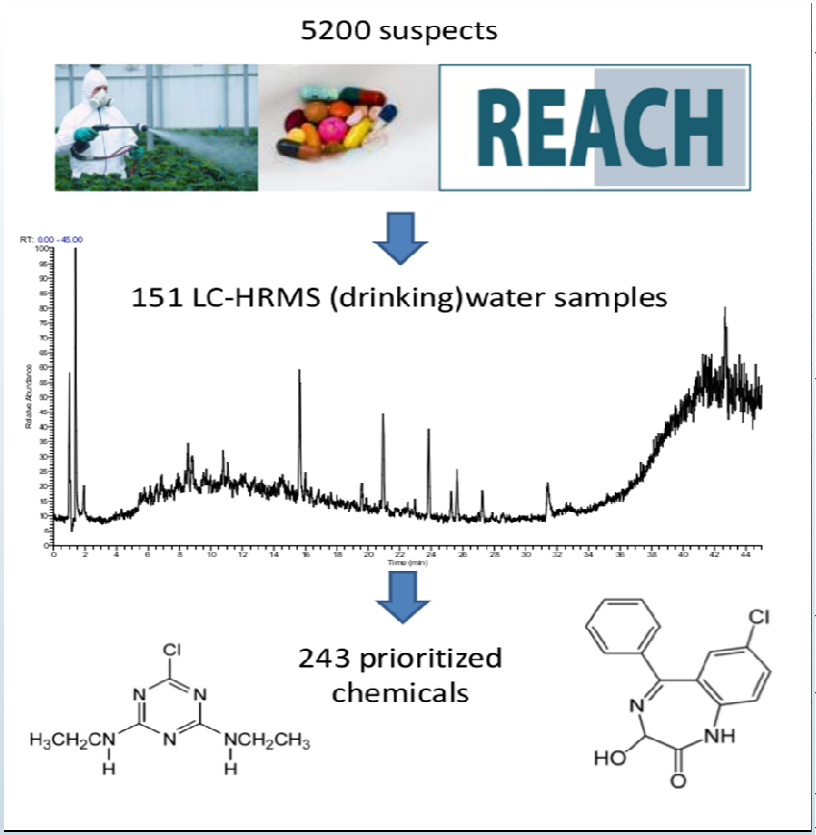
H = 01.00783 P = 30.97376

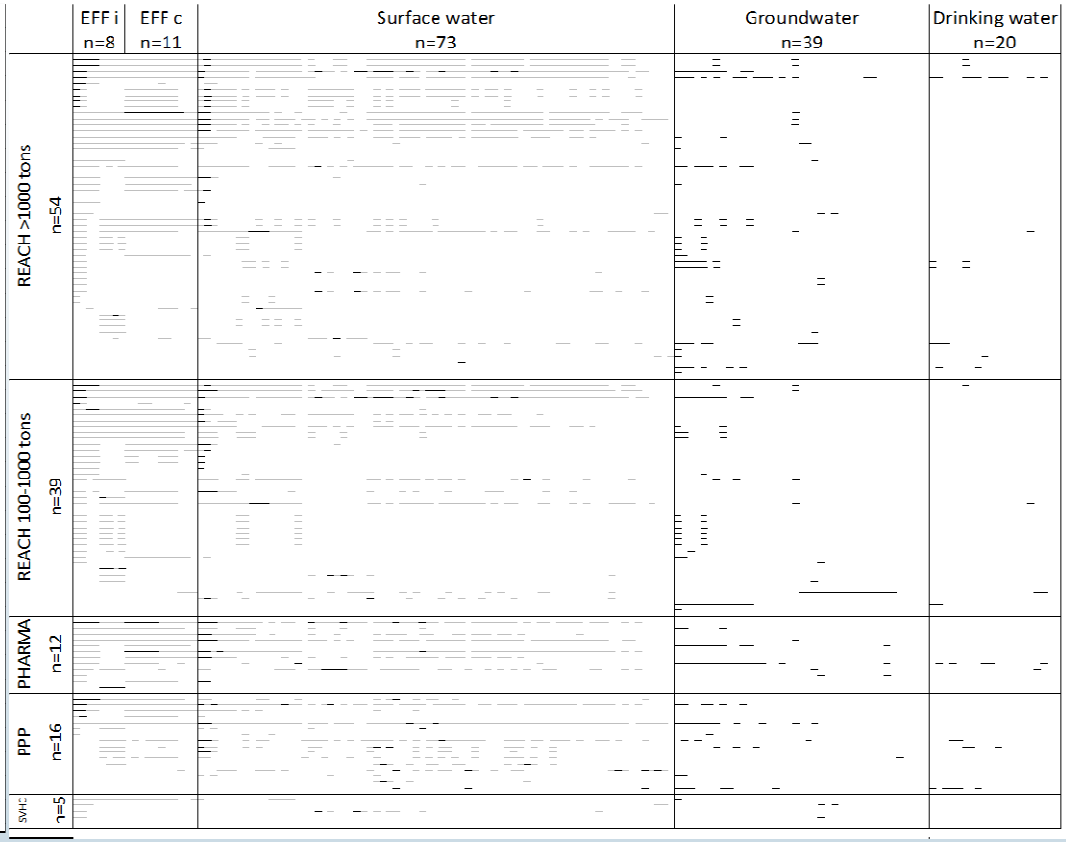
O = 15.99491 F = 18.99840

Massa	Aantal mogelijkheden voor brutoformule
431	~ 10000
431.2	~ 1000
431.20	~ 100
431.199	~ 10
431.1992	~ 1

HOE ACCURATER DE MASSA, HOE ZEKERDER DE BRUTOFORMULE

Suspect screening
waterkwaliteitsprofielen





Sjerps et al. Water Research 93 (2016) 254-264

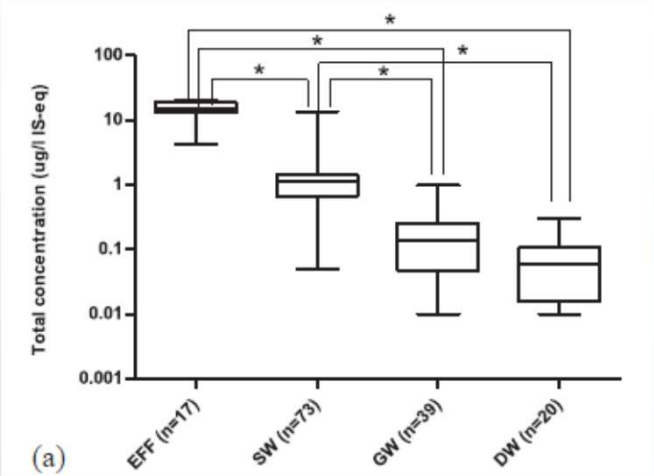
Suspect screening
waterkwaliteitsprofielen

174 prioritized suspects, only 36 mentioned in literature EU target monitoring.

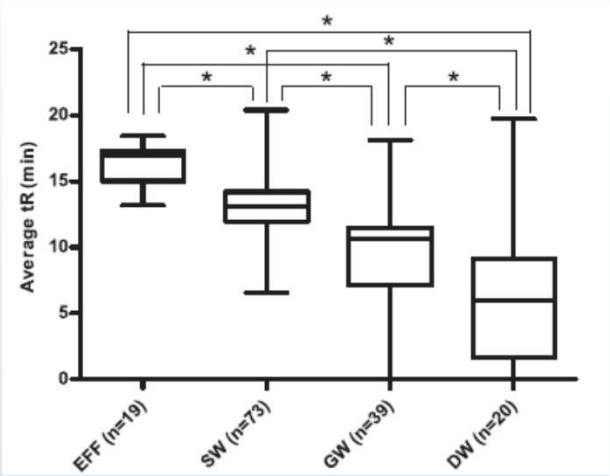
<25% prioritized by NORMAN & IAWR/RIWA

→ suspect screening LC-HRMS complementary to target analysis

→ Further confirmation identity needed



Conc. decrease in watercycle



Polarity increase

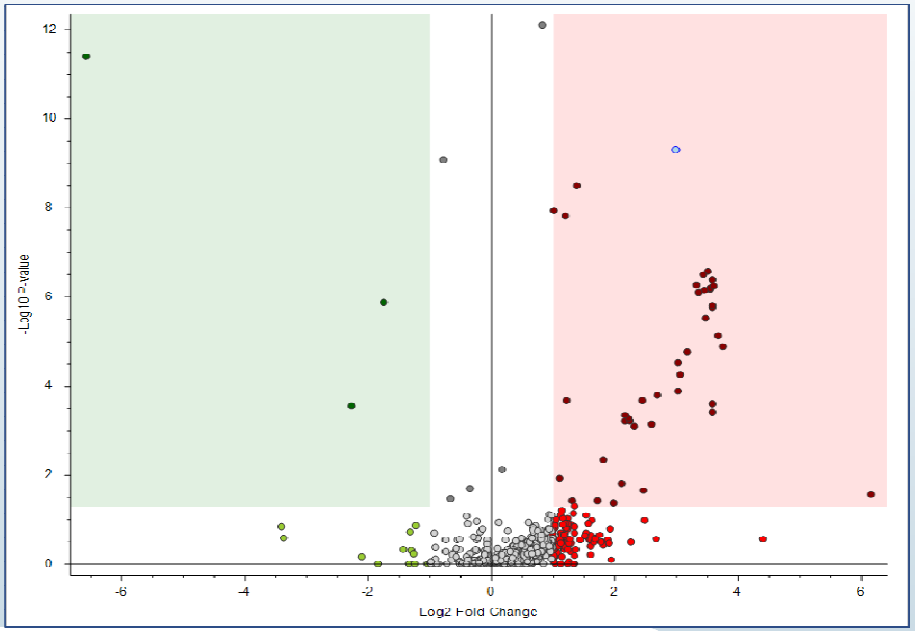
Sjerps et al. Water Research 93 (2016) 254-264

Non-target screening

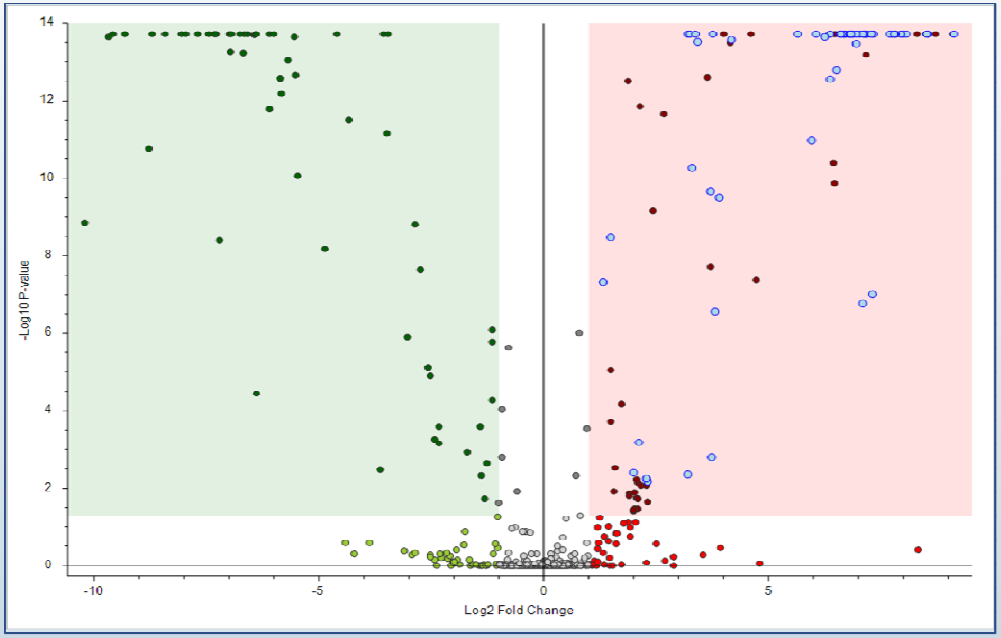
Transformatie producten gevormd tijdens zuivering

Volcano plots: log p-value versus log2 fold change

SAND FILTRATION DAY 0



OZONATION 100UG/L SPIKE-IN, LOW OZONE CONC

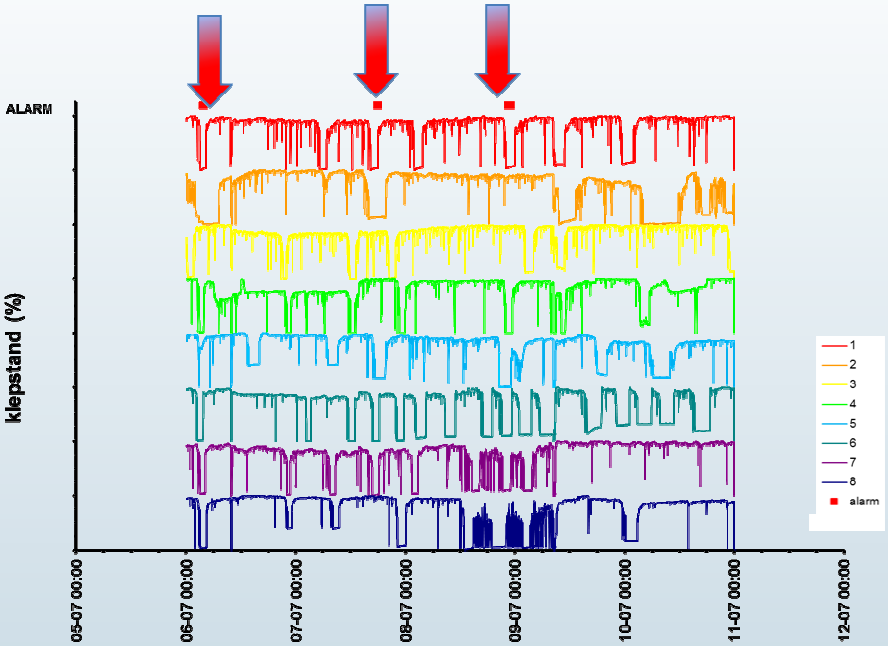


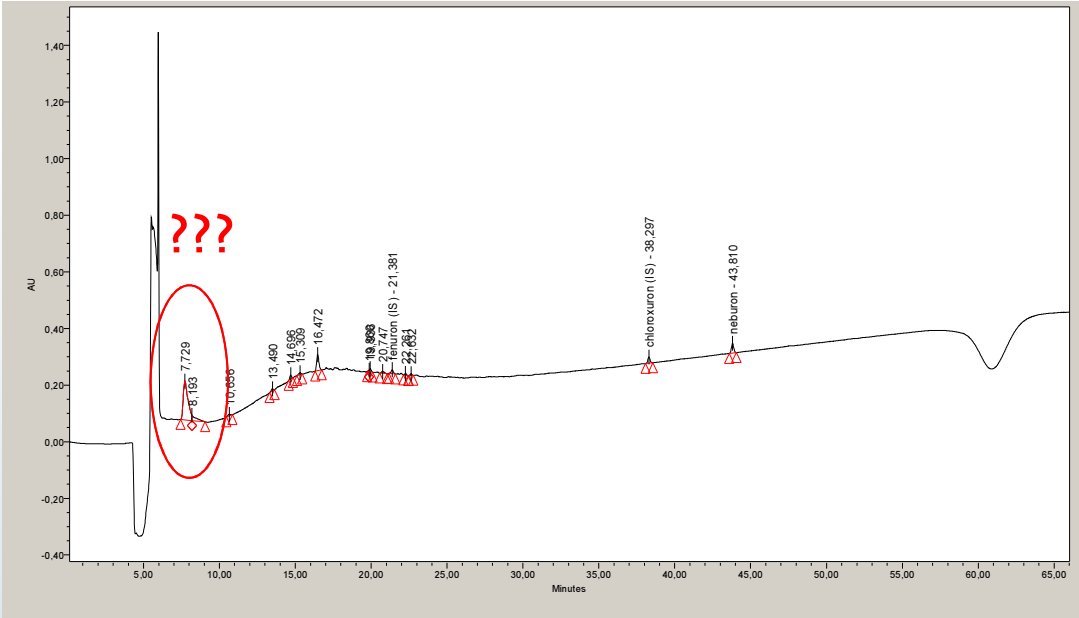
Courtesy: Andrea Brunner KWR

Non-target screening

Identificatie van onbekenden

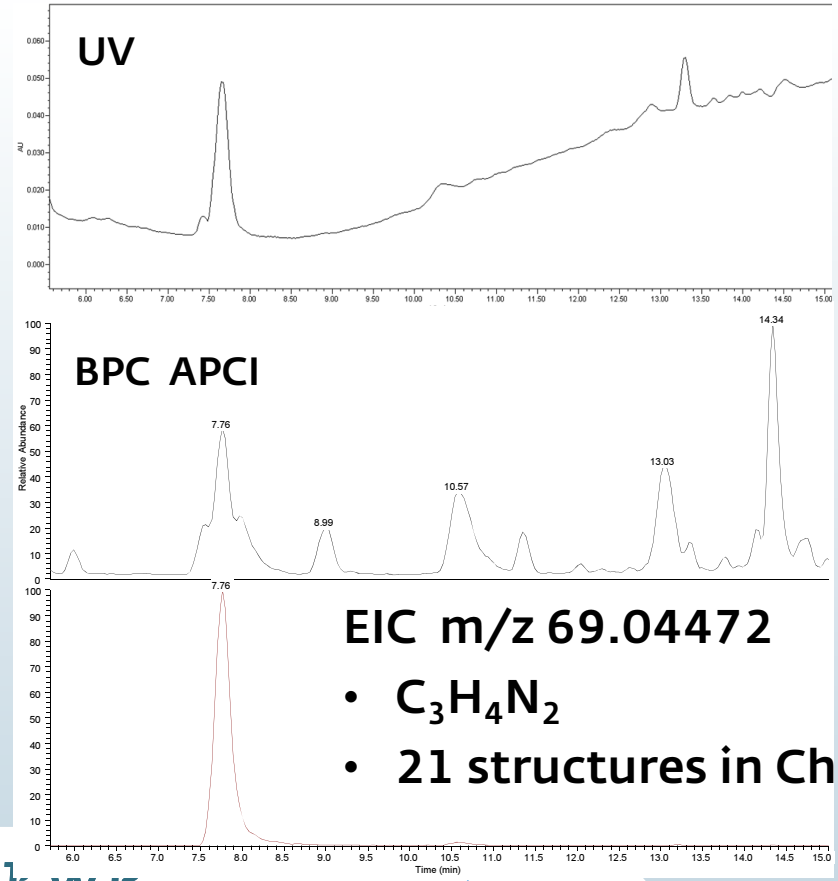
Summer of 2015, alarm in river Meuse

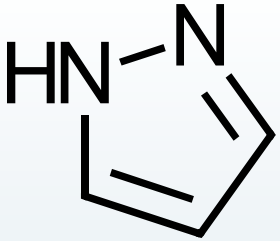




Non-target screening

Identificatie van onbekenden



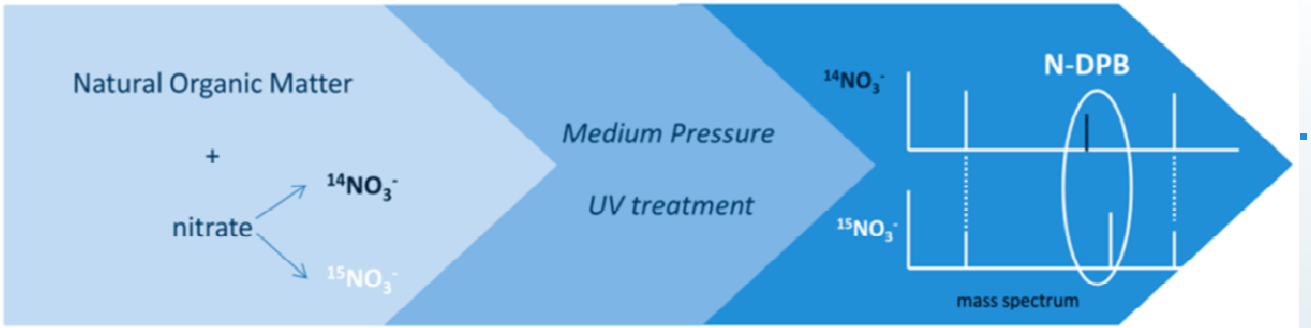


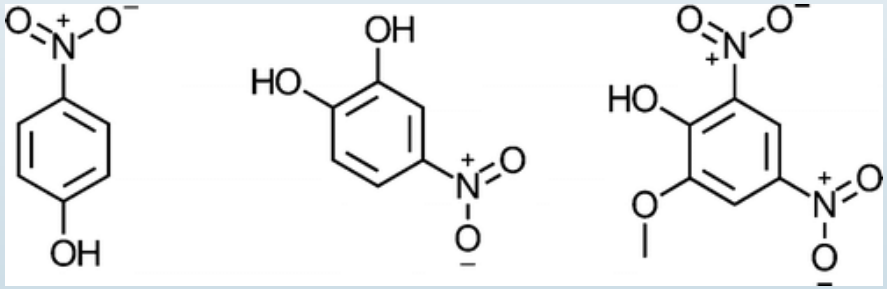
EIC m/z 69.04472

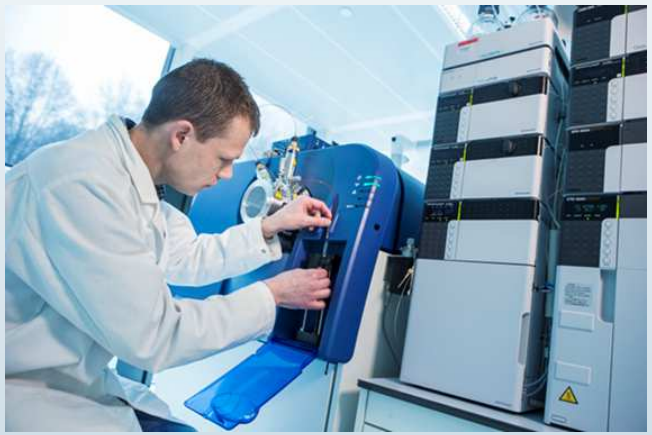
- $C_3H_4N_2$
- 21 structures in Chemspider

Non-target screening

Traceren en identificatie N-DPBs



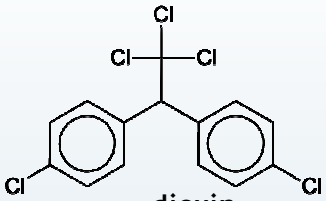




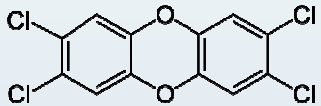
Kolkman et al / ES&T (2015) 4458-4465

Shift
from non-polar to polar environmental contaminants

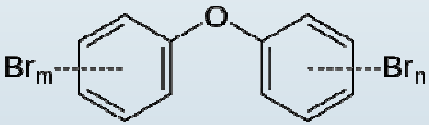
DDT



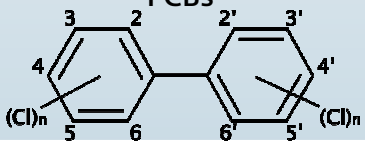
dioxin



BDEs



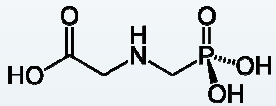
PCBs



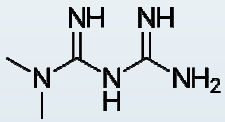
- **Regulation:**
  - ban / restrictions
- **Societal change:**
  - new technologies, products and medications
  - ageing of population
- **Climate change (precipitation):**
  - Non-point source pollution

PFOA

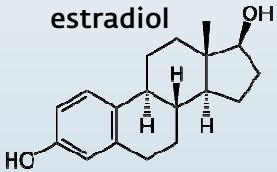
glyphosate



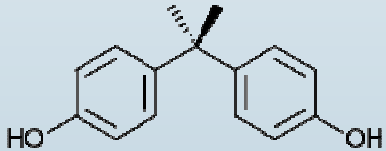
metformin



estradiol



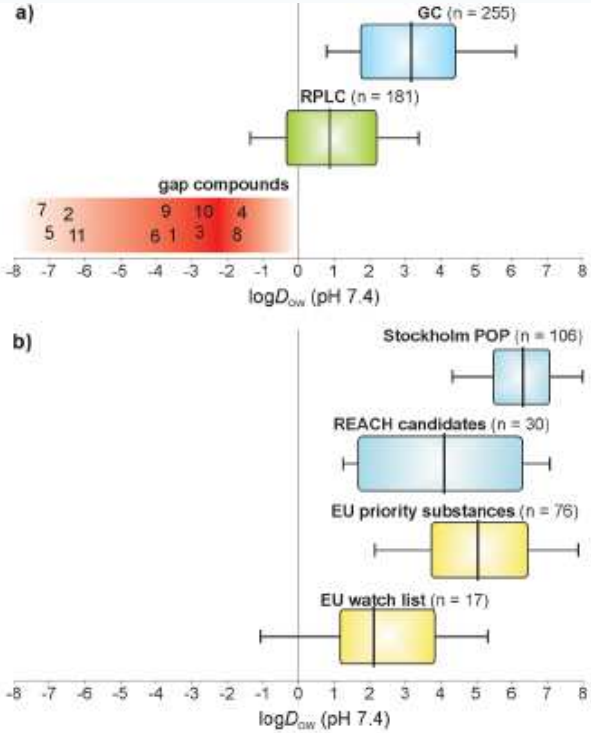
bisphenol A



Trend 2

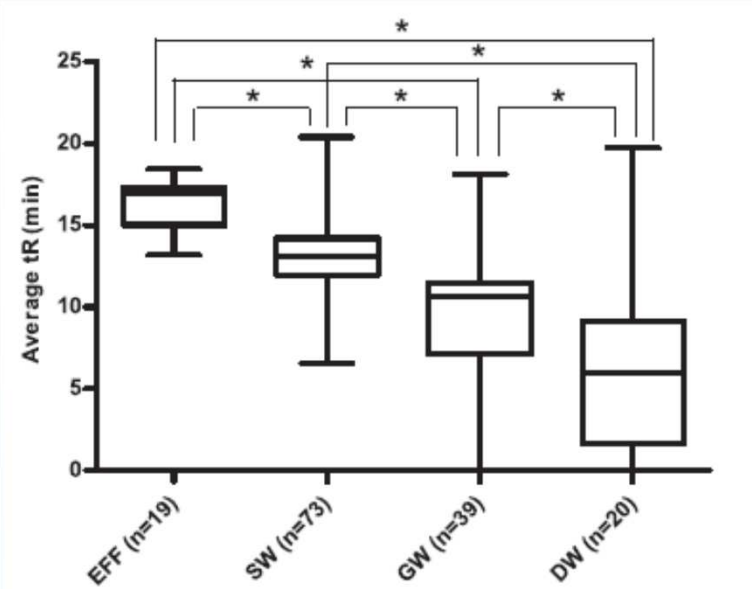
Aandacht voor zeer polaire stoffen

Reemstma et al, ES&T, 2016



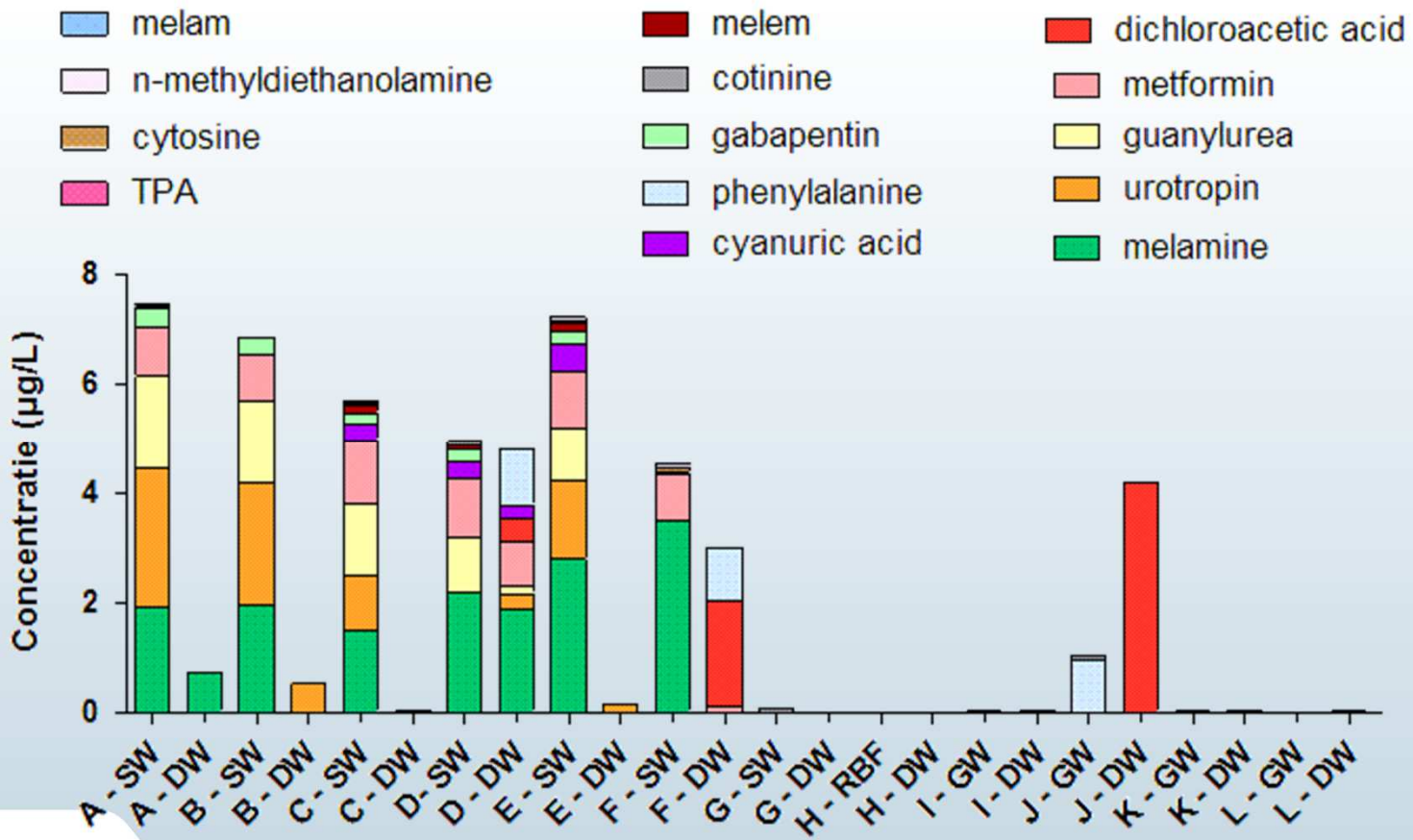
1: AMPA
2: Paraquat
3: Cyanuric acid
4: DMS
5: Diquat
6: 5-Fluorouracil
7: Glyphosate
8: Melamine
9: Metformin
10: Perfluoroacetic acid
11: EDTA

Sjerps et al, Water Research, 2016



Results - HILIC target/non target analyse

Monitoring voor en na zuivering

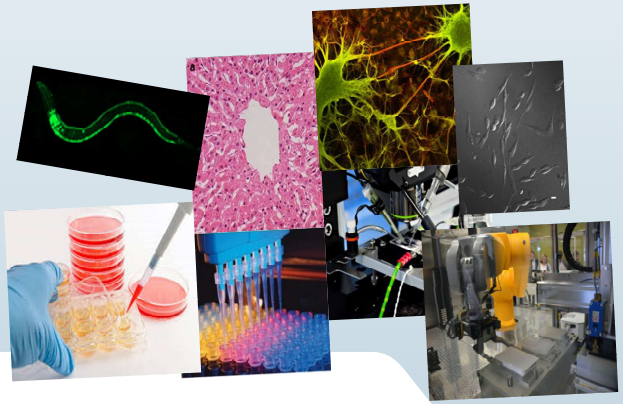


Trend 3
Bioassays - Effect metingen

Effectmeting als maat voor

- aanwezigheid van stoffen
- risico's van stoffen

Wat gebeurt met de werking van cellen en moleculen in aanwezigheid van stoffen?



Toepassingen van bioassays:

- wanneer chemisch-analytisch meten niet vanzelfsprekend is
- voor het testen van de totale respons van alle aanwezige stoffen (en mogelijk mengseleffecten)
- bioassays zijn in sommige gevallen meer gevoelig dan chemische analyses

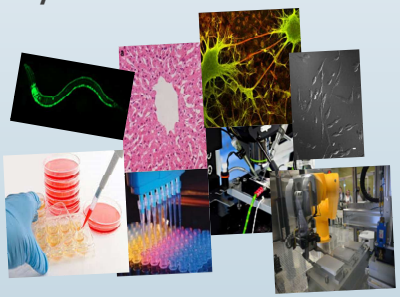
Bioassays

Eindpunten voor waterkwaliteit

- DNA schade / reactieve effecten (Ames test)
- Effecten op hormoonsystemen (Calux)
- Effecten op metabolisme van lichaamsvreemde stoffen
- Adaptieve stress responsen (bijvoorbeeld reactie op oxidatieve stress)
- Effecten op ontwikkeling en reproductie
  - *Hiervoor zijn nog weinig bioassays*

Uitdagingen

- recente innovaties (nieuwe tools)
- interpretatie
  - effect-signaalwaarden (trigger values)
  - mengseltoxicologie (effect door gecombineerde blootstelling?)
- andere effecten?
  - zenuwstelsel en immuunsysteem
  - opkomende stoffen



Bioassays

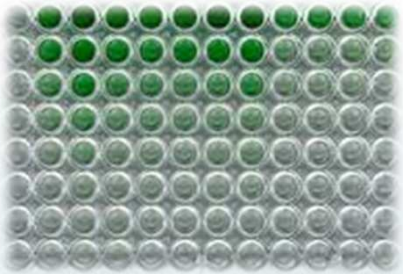
Looking to effects of (mixtures of) chemicals

Water sample

Drinking water
Waste water
Surface water
Treated water
Water extracts
….

Expose cells

Bacteria
Yeast
Mammalian cells
Human cells
Embryonic cells
Stem cells
Co-cultures
Tissues

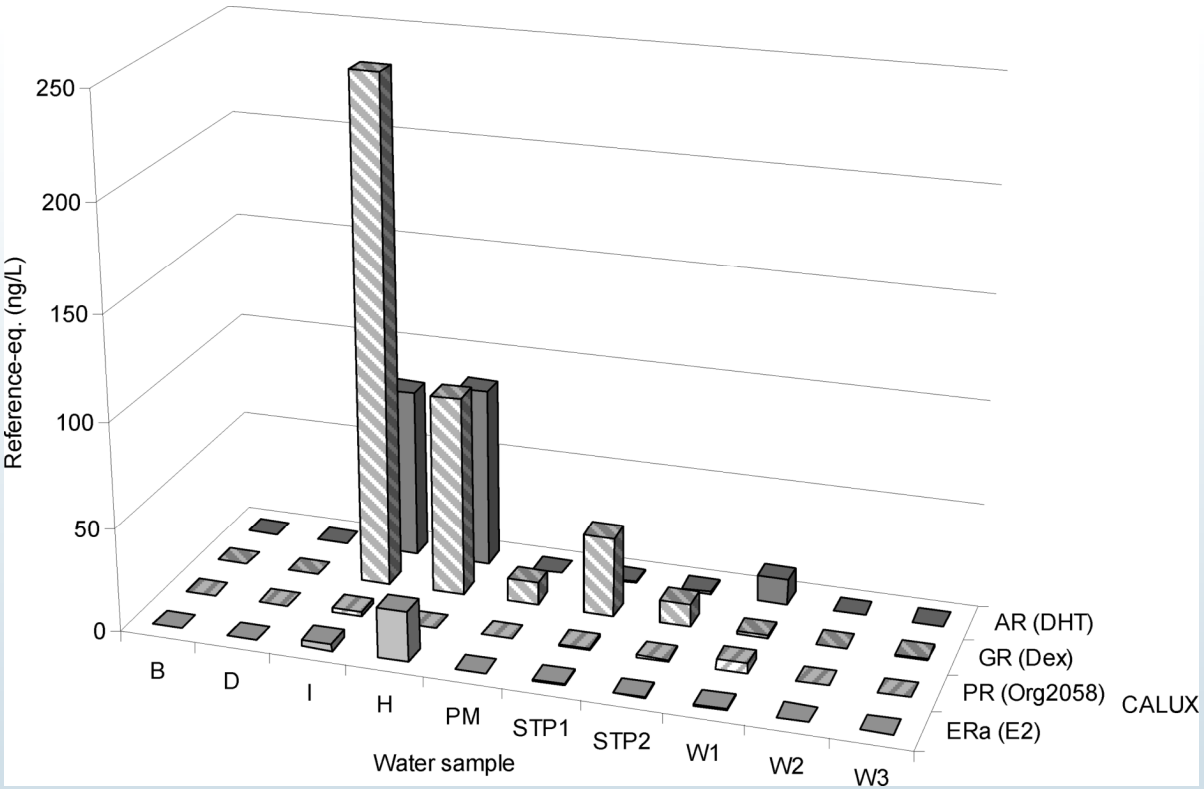


Measure effect

Cell growth
Colorimetric
Luminescence
Fluorescence
Flow cytometry
Receptor binding
Gene expression
….

Bioassays - effects

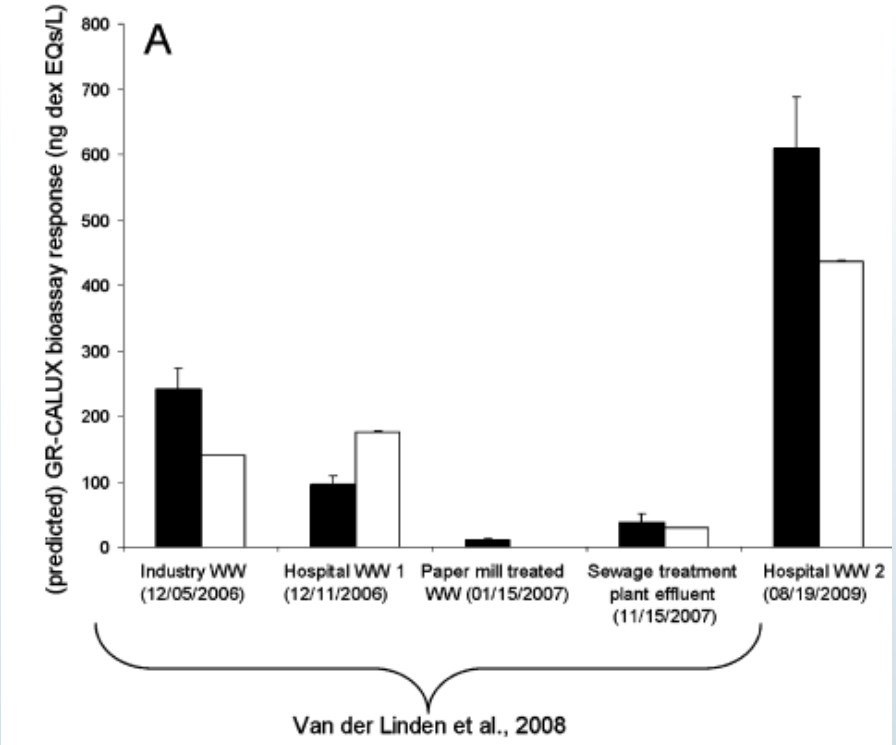
Water samples – Endocrine disruption



Van der Linden *et al.*, ES&T (2008) 5814-5820

Bioassays - effects

Effect metingen - water samples – Endocrine disruption



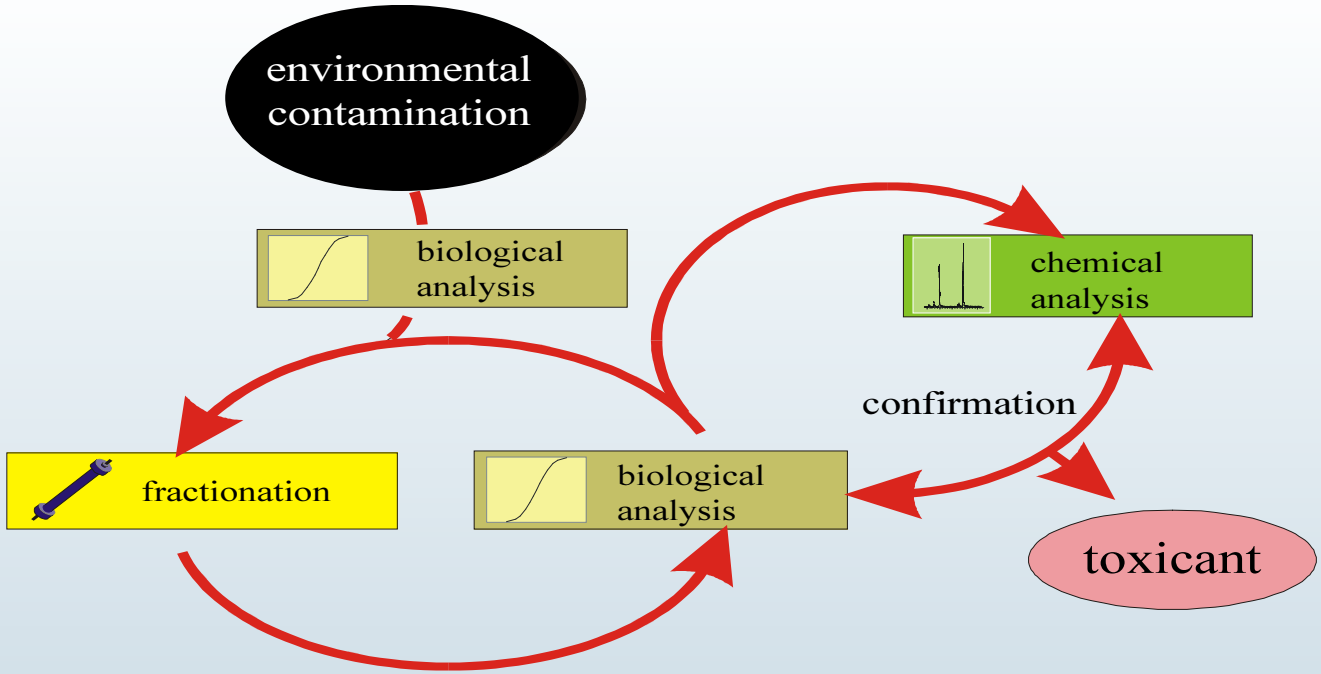
Measured GR CALUX bioassay response

"Predicted" GR CALUX bioassay response

Schriks et al ES&T (2010), 44, (12), 4766-4774

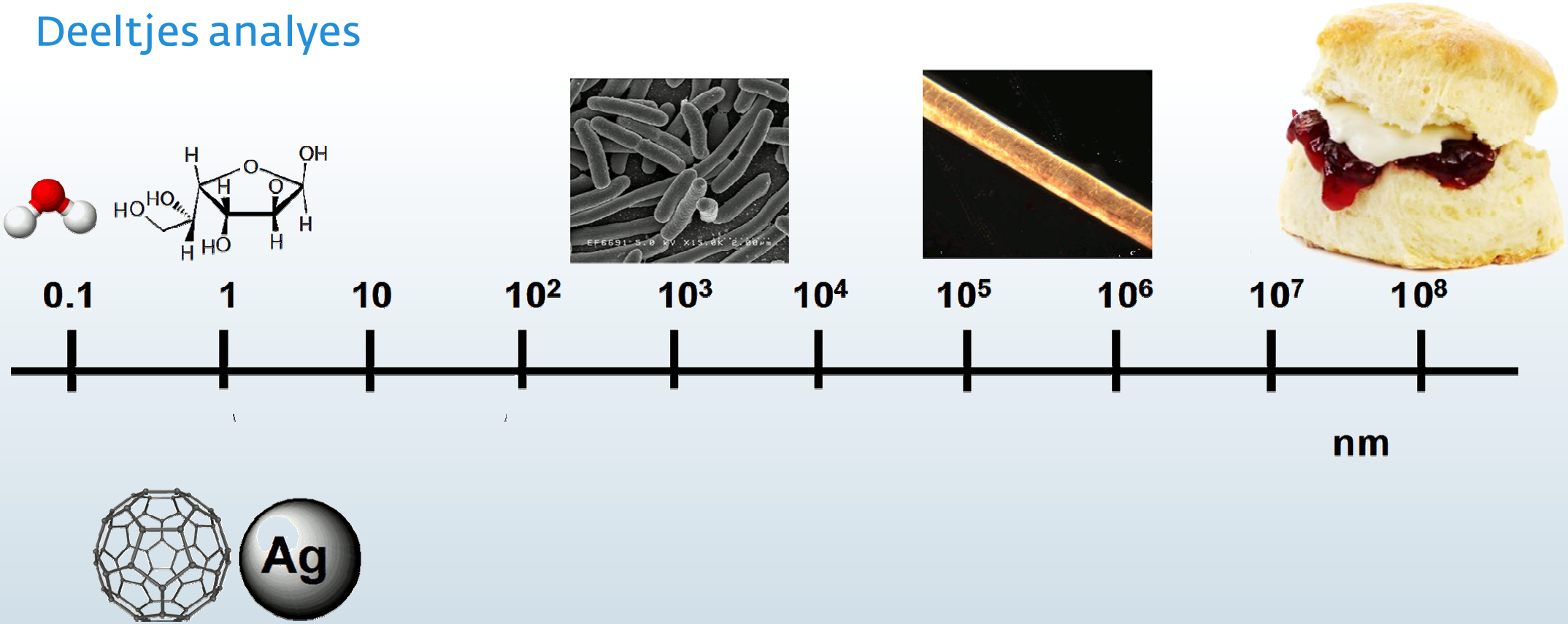
Combination bioassays – analytical chemistry

The best of both world…..s



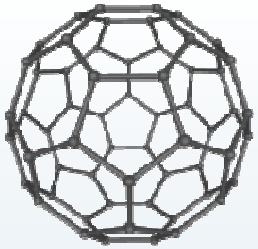
http://www.ufz.de/eda-emerge/

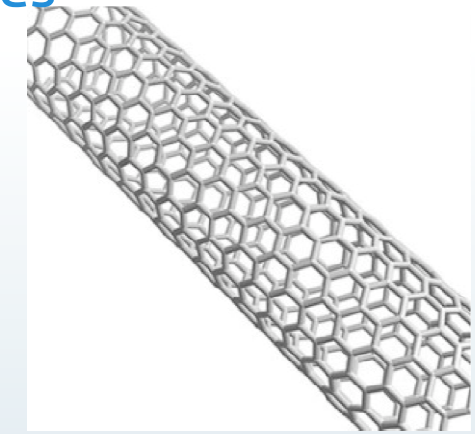
Trend 4
Deeltjes analyes

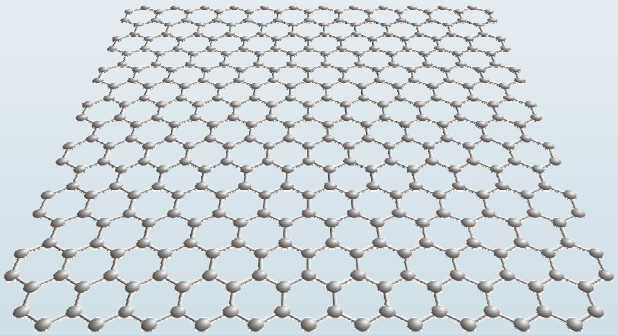


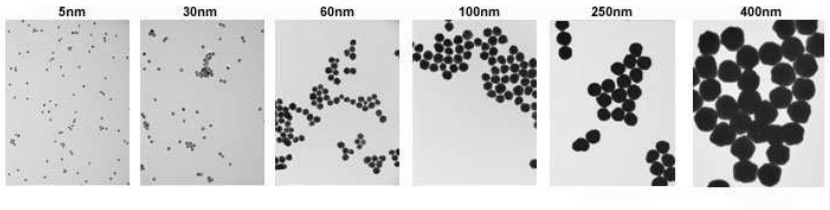
Deeltjes analyse

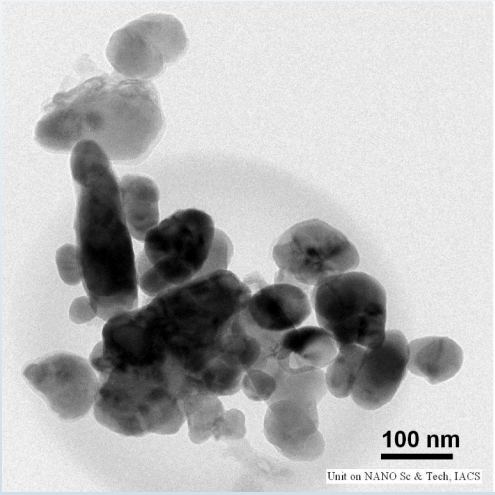
nanodeeltjes





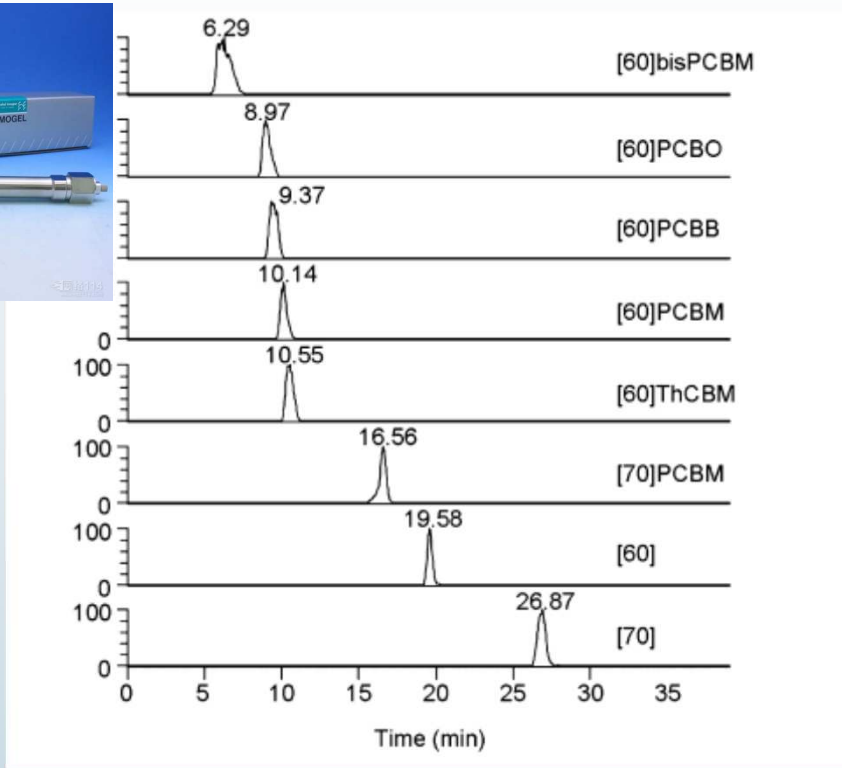


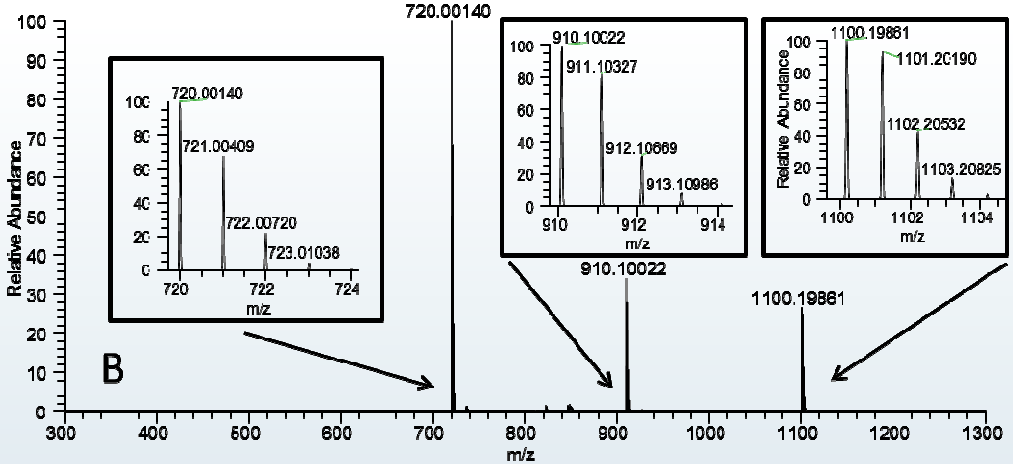


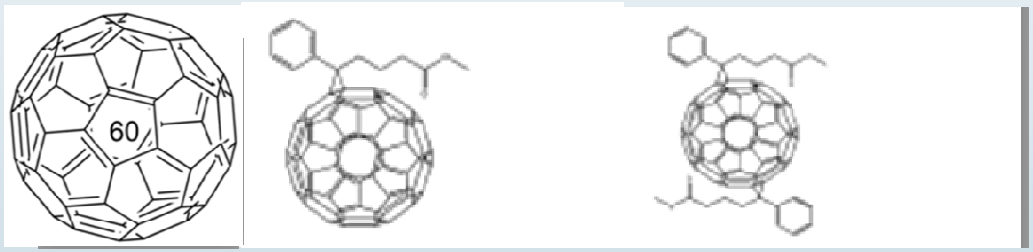


Deeltjes analyse

Nanodeeltjes – fullerenen - HPLC Orbitrap MS



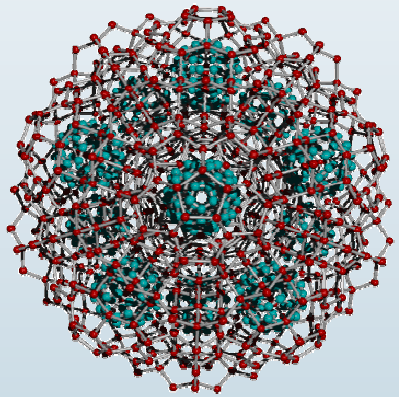


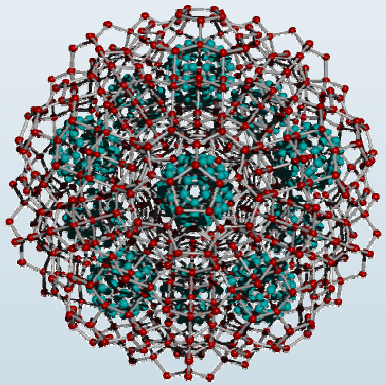


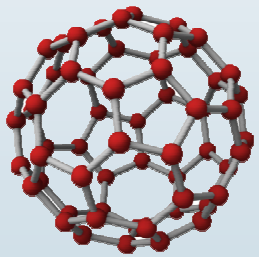
Kolkman et al, Analytical Chemistry, 2013, 5867-5874

Deeltjes analyse

Nanodeeltjes – fullerenen - FFF scheiding van C60 clusters

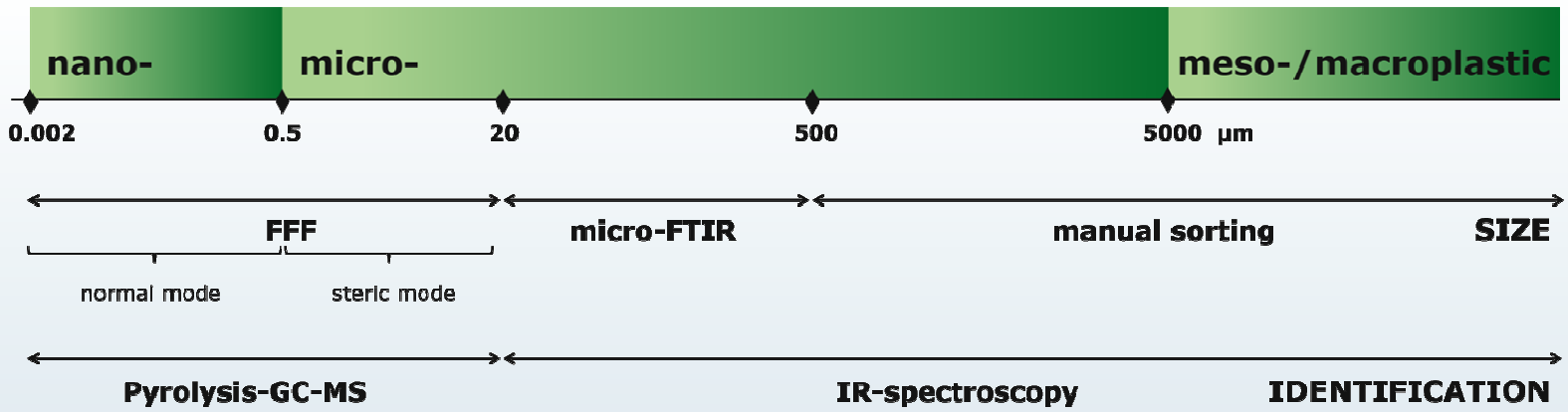


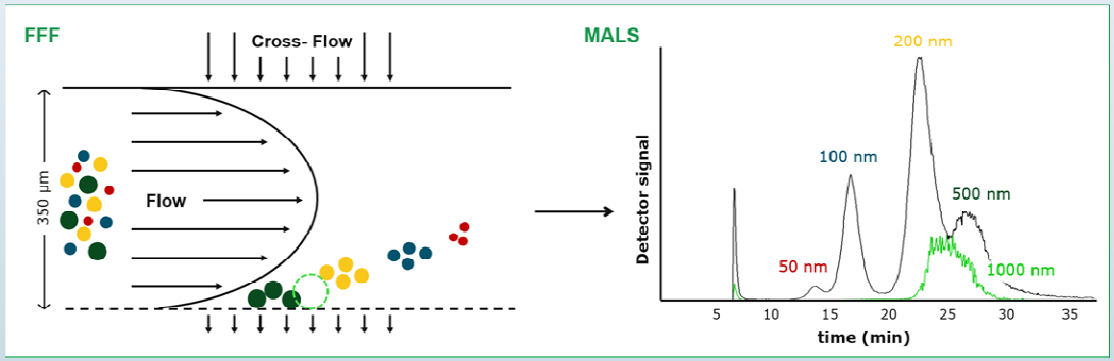




Deeltjes analyse

Micro/nanoplastics: Closing the gap between small and smaller





Tenslotte
Trends in chemische analyes

Nieuwe tools (non target screening, analyse zeer polaire stoffen, bioassays, deeljesmetingen) zijn leuk voor een analytisch chemicus; maar toepassing in een relevant vraagstuk is nog interessanter:

- Verstoring bij een RWZI, wat is de oorzaak?
- Welke transformatieproducten worden gevormd in een zuivering?
- Kwaliteit van afvalwater, struviet, regeneraat, calciet, ect.,.
- Monitoring (tijd, ruimte)
- Uw favoriete vraagstuk
- ……
- ect

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