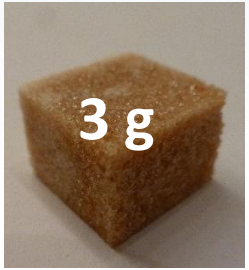
A validated SBSE-GC-MS/MS method for ultra-trace analysis of priority pollutants in surface water in the context of the EU water framework directive with additional focus on suspended matter

Oliver Lerch, Jasmin Zboron
GERSTEL GmbH & Co. KG
Muelheim, Germany
Oliver_Lerch@gerstel.de

September 24th 2019

5TH SBSE INTERNATIONAL MEETING
23 & 24 SEPTEMBRE 2019 - NOVOTEL PARIS-SUD
SBSE Technical Meeting


3 g


~0,4 ng/L im Baldeneysee

Joint Project of Agilent and Gerstel

Stuart Miles, freedigitalphotos.net

Many thanks to the following Agilent colleagues

Juan-Luis Aybar

John Upton

Tarun Anumol

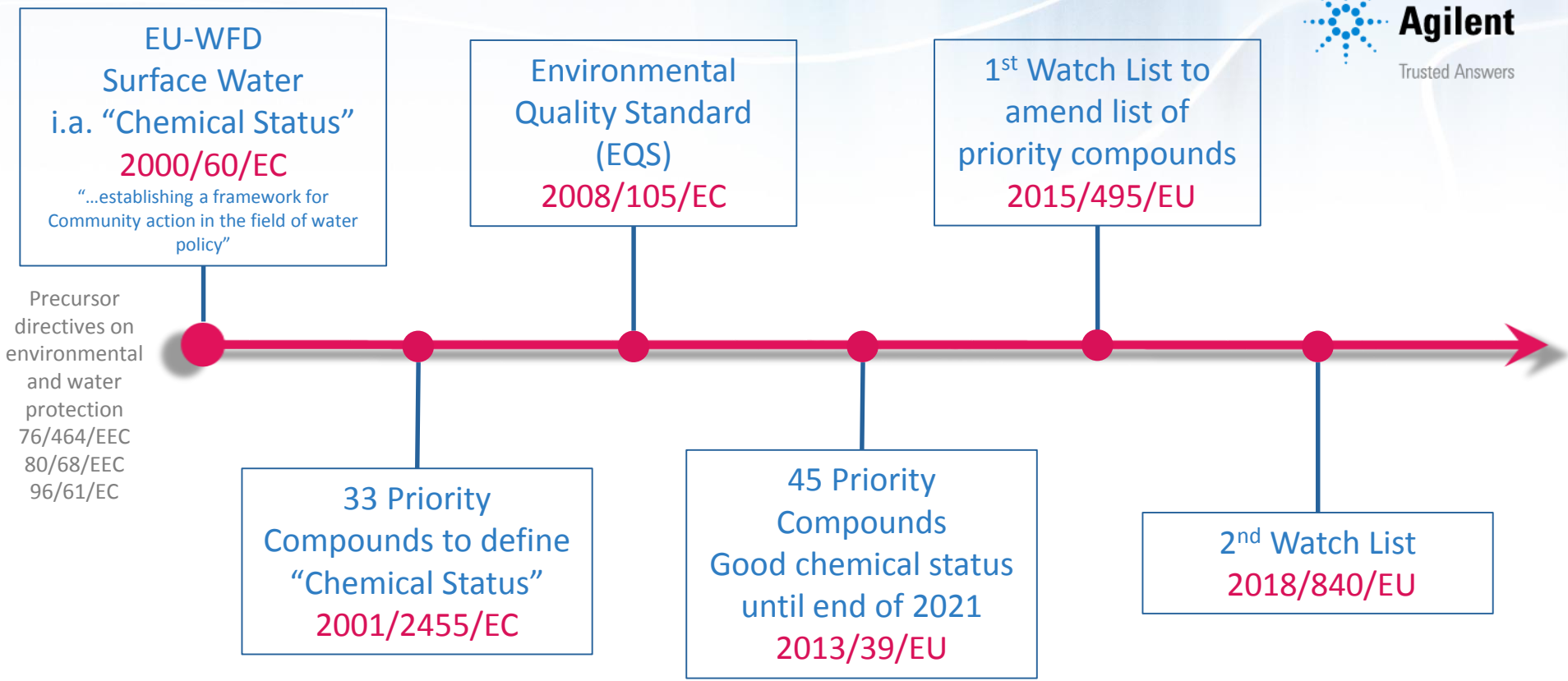
Ken Brady

Alain Vervaecke

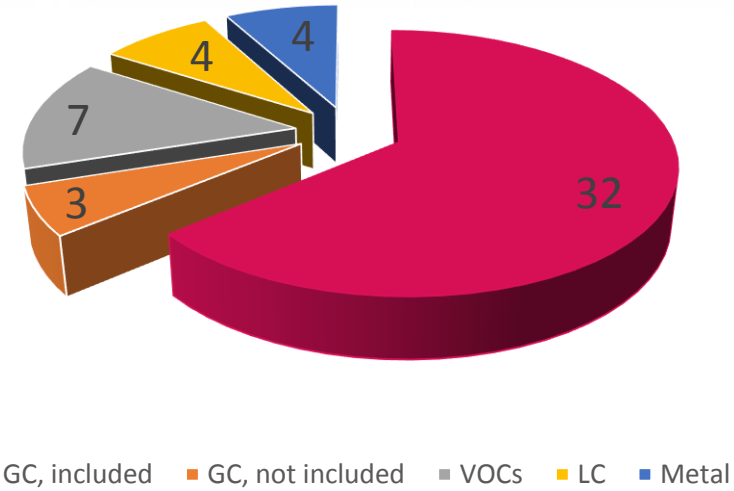
Many thanks to the following GERSTEL colleague

Jasmin Zboron

Background on
EU Water Framework Directive (EU-WFD)

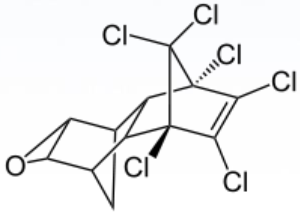

EU-WFD
Surface Water
i.a. "Chemical Status"
2000/60/EC
"…establishing a framework for Community action in the field of water policy"
Precursor directives on environmental and water protection
76/464/EEC
80/68/EEC
96/61/EC
33 Priority Compounds to define "Chemical Status"
2001/2455/EC
Environmental Quality Standard (EQS)
2008/105/EC
45 Priority Compounds
Good chemical status until end of 2021
2013/39/EU
1st Watch List to amend list of priority compounds
2015/495/EU
2nd Watch List
2018/840/EU

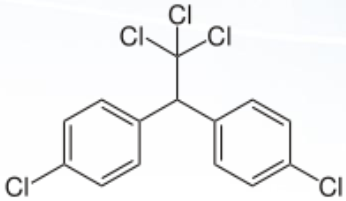
Priority Compounds(-Groups) EU-WFD

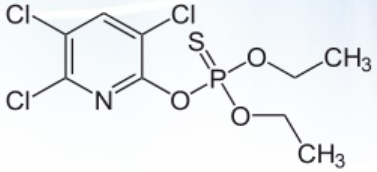


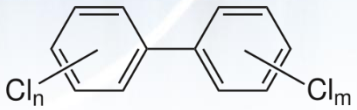
- **GC compatible, included ~70% of compounds:**
  - Around 100 compounds
    32 compound groups & individual compounds from EU-WFD
    Country specific relevant compounds for surface water analysis
- **GC compatible, not included:**
  - C10-C13 Chloroalkanes:
    dedicated method needed
  - Tributyltin:
    dedicated method needed (e.g. RIC Belgium)
  - Dioxins:
    could be included, but not in our lab
- **VOCs:**
  - Dedicated headspace GC-MS/MS method to be developed
- **LC compatible:**
  - Diuron, isoproturon, hexabromocyclododecane, PFOS
- **Metals:**
  - With AAS or ICP-MS

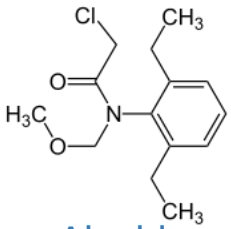
Choice of Analytes from 2013/39/EU

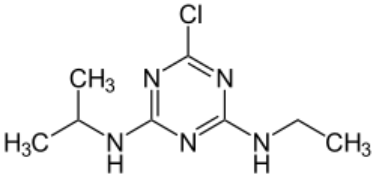

Dieldrin

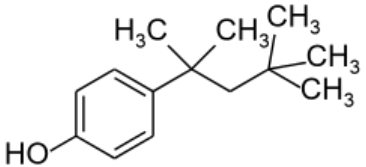

p,p´-DDT

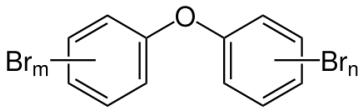

Chlorpyrifos

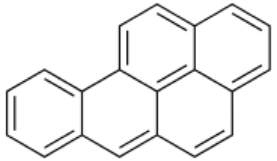

PCBs

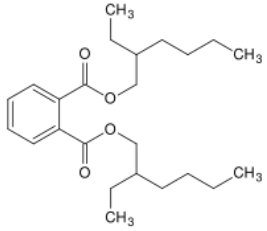

Alachlor

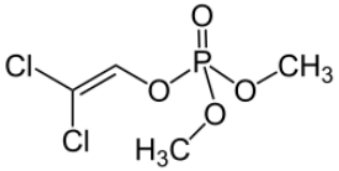

Atrazine

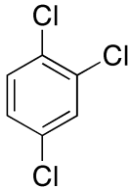

4-tert-Octylphenol


PBDEs


Benzo[a]pyrene


Diethylhexylphthalate


Dichlorvos


1,2,4 Trichlororobenzene

Challenges

- Numerous differing compounds
- Low required LOQs
  derived as 0.3x the respective annual average EQS: e.g. 600 ng/L naphthalene, p,p´-DDT 3 ng/L, endosulfan 1.5 ng/L, dichlorvos 0.18 ng/L, benzo[a]pyrene 0.051 ng/L, 0.024 ng/L cypermethrine, 0.06 pg/L heptachlor and heptachlor epoxide
- “Where those criteria are not met for any matrix, Member States shall ensure that monitoring is carried out using best available techniques not entailing excessive costs”
- “Concentrations in the whole water sample”
  -> Extraction of particle adsorbed compounds required

Stir Bar Sorptive Extraction (SBSE)
GERSTEL Twister (PDMS)

Twister Extraction

1 cm Twister

Add conditioned Twister to sample vial

Parallel extraction – partitioning of the analytes between water and PDMS phase

Removal of Twister after extraction

Removal of residual sample and particles by dipping into clean water

Transfer to clean TDU desorption tube

Drying in N_2 stream, alternatively by clean and lint free tissue

Ready to put into autosampler tray

Thermal Desorption Unit

TDU

100 % analyte transfer
onto column is possible

Cooled Injection System as
„Cryotrap“

CIS

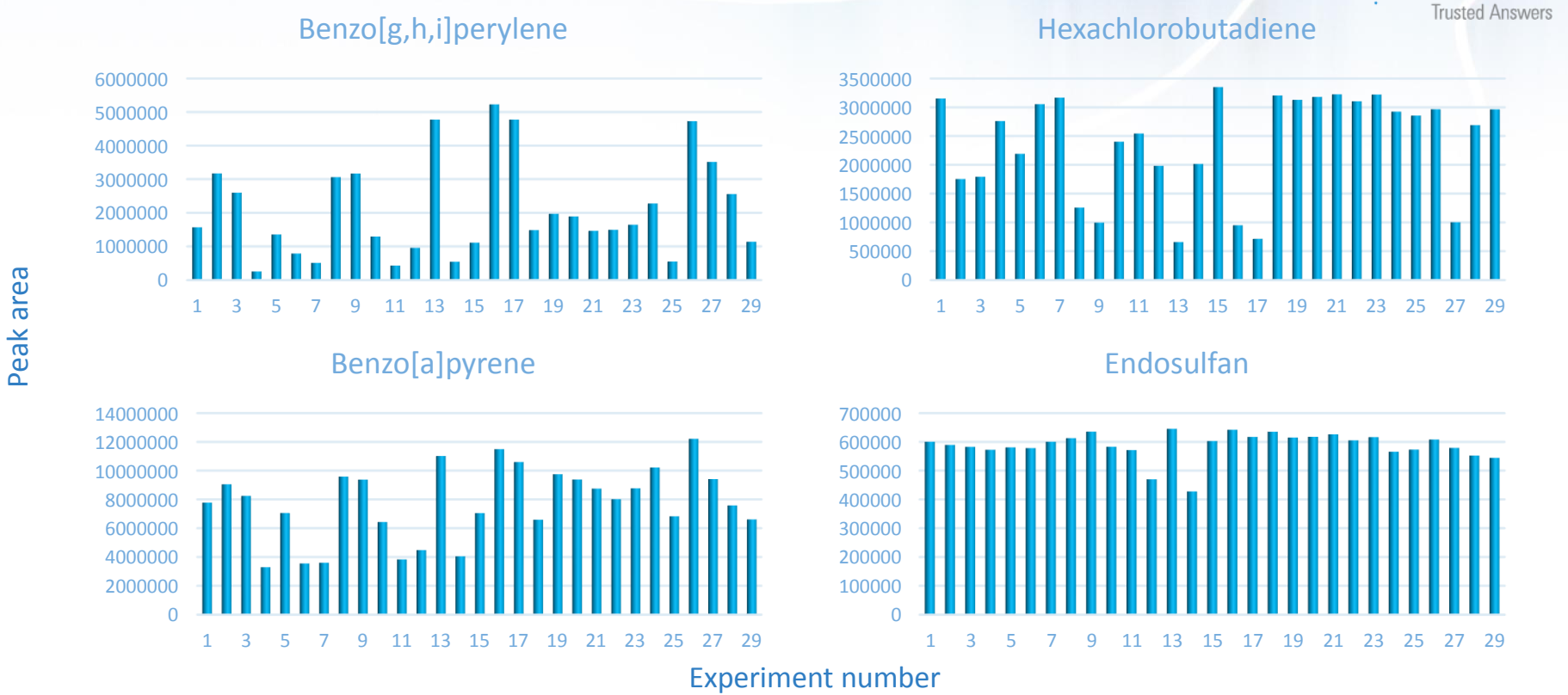
Optimization of Sample Preparation Method

Method Optimization – TDU/CIS Parameters

- Statistical design of experiments
- 29 experiments with different combinations of parameter values
- Experiment 1, 15, 29 “center points” with average parameter values
- CIS splitless time and further optimization with optimized TDU/CIS parameters

Parameter	Minimum	Maximum
TDU final temperature [°C]	250	300
TDU hold time [min]	3	10
TDU heating rate [°C/min]	80	250
Desorption flow [mL/min]	30	80
CIS trapping temperature [°C]	-30	-100

Method Optimization – TDU/CIS Parameters

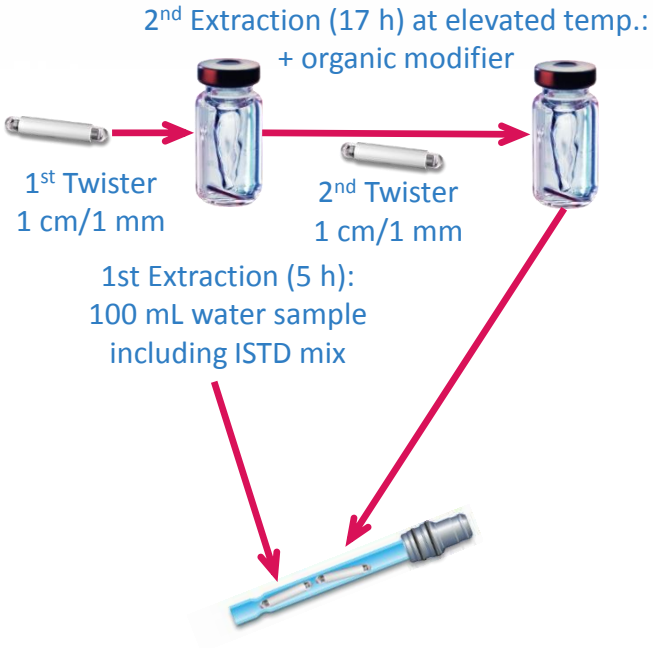


Sample Prep Solution Method

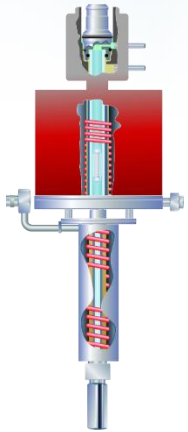
GERSTEL

Agilent
Trusted Answers

Sample Preparation



Thermal Desorption



Thermal Desorption Unit
(TDU, 90 – 300 °C)
Valveless Cooled Injection System
(CIS, -40 – 300 °C)
TDU Solvent Vent 2 min at 90°C

GC-MS/MS

7890/7010
HP-5ms UI 30m, 0.25 mm, 0.25 µm
60 °C, 1 min, 40 °C/min, 120 °C , 5 °C/min, 310 °C, 10 min
RTL chlorpyrifos-methyl
MRM

e.g. 100 pg/L in 100 mL sample → 10 pg per injection

Reduced Sample Volume!

GERSTEL

Agilent

Trusted Answers

Standard water analysis method
0.5 - 1 L

Twister method
0.1 L

How does the developed Method perform?

Limits of Quantification (LOQ)

LOQ determination according to DIN 32645 and under consideration of precision and trueness. If possible extracted from river water.

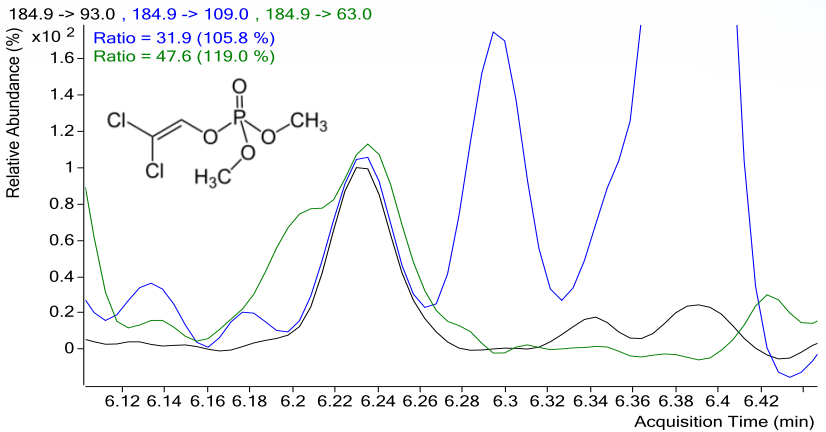
Analyte	LOQ [ng/L]
Acenaphthene	1.0
Acenaphthylene	0.10
Aclonifen	0.56
Alachlor	0.42
Aldrin	0.066
Ametryn	0.069
Anthracene	0.061
Atrazine	0.18
Benz[a]anthracene	0.076
Benzo[a]pyrene	0.033
Benzo[b]fluoranthene	0.078
Benzo[g,h,i]perylene	0.049
Benzo[k]fluoranthene	0.081
Bifenox	0.47
Biphenyl	9.0
Bis(2-ethylhexyl)phthalate (DEHP)	134
Chlordane, cis	0.052
Chlordane, trans	0.026
Chlorfenvinphos	0.084
Chlorpyrifos-ethyl	0.024
Chrysene	0.027
Cybutryne (Irgarol 1051)	0.030
Cypermethrine (4 isomers)	0.12
p,p´-DDD	0.020
p,p´-DDE	0.017
o,p´-DDT	0.052
p,p´-DDT	0.067
Dibenz[a,h]anthracene	0.073
Dichlobenil	2.1
Dichlorvos	0.073
Dicofol	0.15
Dieldrin	0.034
Diflufenican	0.16
2,6-Di-tert.-butyl-4-methylphenol	5.9

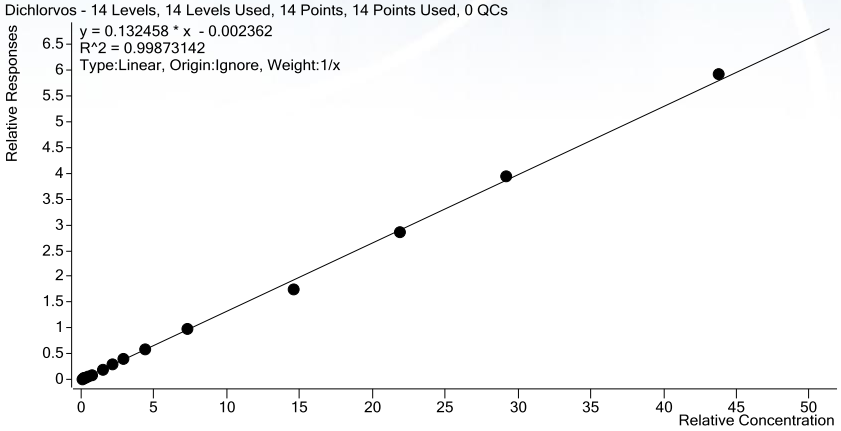
Analyte	LOQ [ng/L]
alpha-Endosulfan	0.070
beta-Endosulfan	0.059
Endosulfan sulfate	0.052
Endrin	0.043
Endrin ketone	0.052
Ethofumesate	0.073
Fenitrothion	0.024
Fenpropimorph	0.13
Fluoranthene	1.0
Fluorene	0.45
Heptachlor	0.052
Heptachlor epoxide	0.052
Hexachlorobenzene	0.10
Hexachlorbutadiene	0.043
alpha-Hexachlorocyclohexane	0.052
beta-Hexachlorocyclohexane	0.13
gamma-Hexachlorocyclohexane	0.052
delta-Hexachlorocyclohexane	0.052
Indeno[1,2,3-cd]pyrene	0.044
Isodrin	0.16
Methoxychlor	0.083
Metolachlor	0.064
Naphthalene	5.0
Nonylphenol	8.8
Octylphenol	0.46
Oxadiazon	0.082
PBDE 28	0.018
PBDE 47	0.015
PBDE 99	0.050
PBDE 100	0.011
PBDE 153	0.032
PBDE 154	0.020
PBDE 183	0.13
PCB 77	0.041

Analyte	LOQ [ng/L]
PCB 81	0.039
PCB 105	0.043
PCB 114	0.036
PCB 118	0.012
PCB 123	0.037
PCB 126	0.050
PCB 156	0.046
PCB 157	0.047
PCB 167	0.044
PCB 169	0.054
PCB 189	0.054
Pendimethalin	0.094
Pentachlorobenzene	0.075
Pentachlorophenol	3.0
Phenanthrene	2.5
Picolinafen	0.26
Prometon	0.18
Prometryne	0.13
Propazine	0.057
Propiconazole	0.14
Propyzamide	0.35
Pyrene	0.45
Quinoxyfen	0.087
Simazine	1.9
Terbutryne	0.1
Triallate	0.084
Tri-n-butyl phosphate	9.7
1,2,3-Trichlorobenzene	0.95
1,2,4-Trichlorobenzene	1.2
1,3,5-Trichlorobenzene	0.18
Triclosan	1.4
Trifluralin	0.19
Tris(2-chloroisopropyl)phosphate (TCPP)	29

Uncertainty of measurments below 50 % for all EU-WFD compounds at or near the respective EQS as required by 2009/90/EC

Dichlorvos – River Water



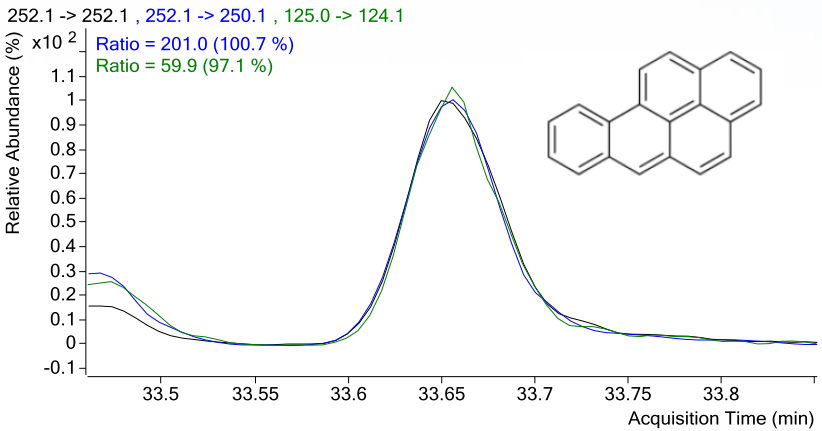


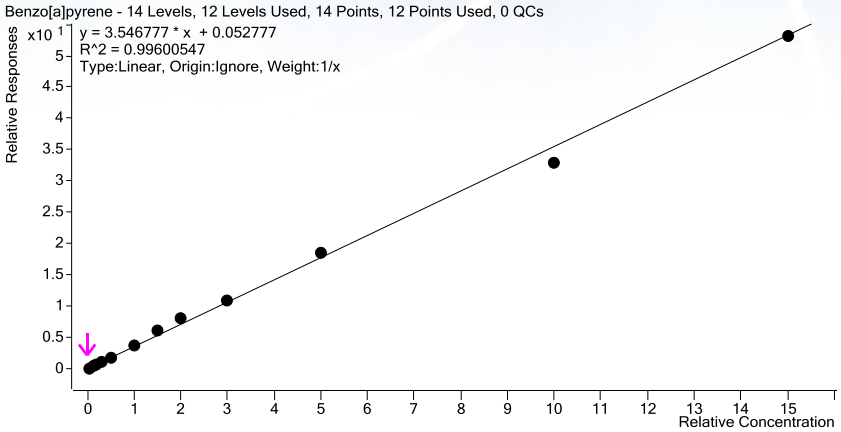
0.073 ng/L in river water, LOQ 0.073 ng/L

7.3 pg on column (100 mL sample, assumption 100% recovery)

Required LOQ 0.18 ng/L (inland surface water)

Benzo[a]pyrene – Mineral Water



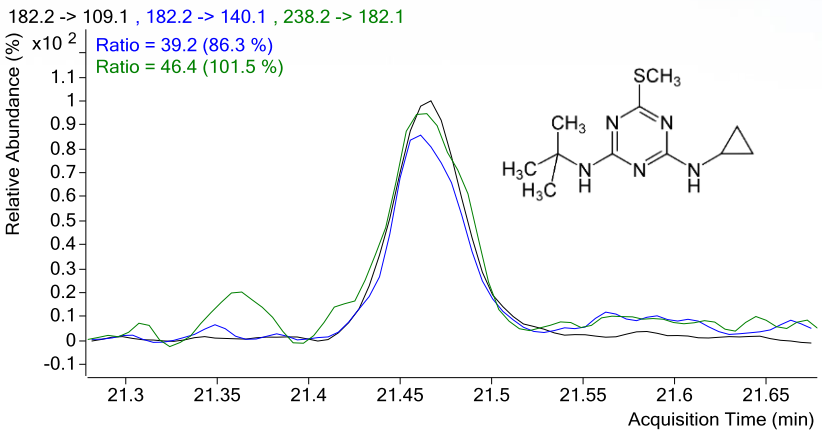


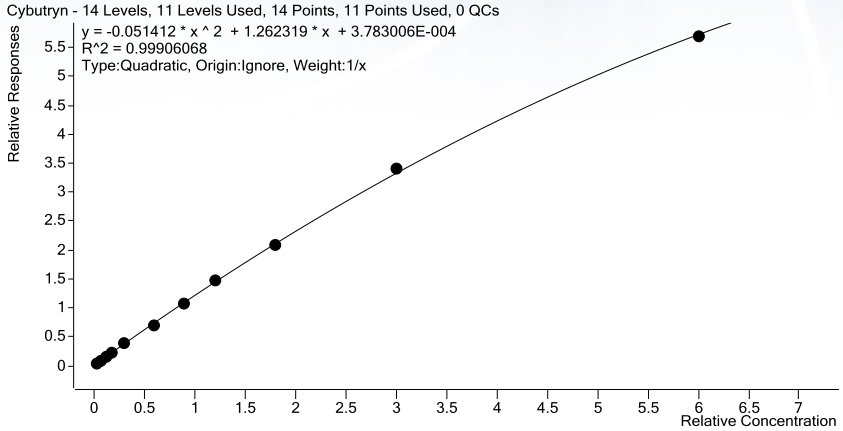
0.040 ng/L in mineral water, LOQ 0.033 ng/L

4 pg on column (100 mL sample, assumption 100% recovery)

Required LOQ 0.051 ng/L (inland surface water)

Cybutryne – Mineral Water



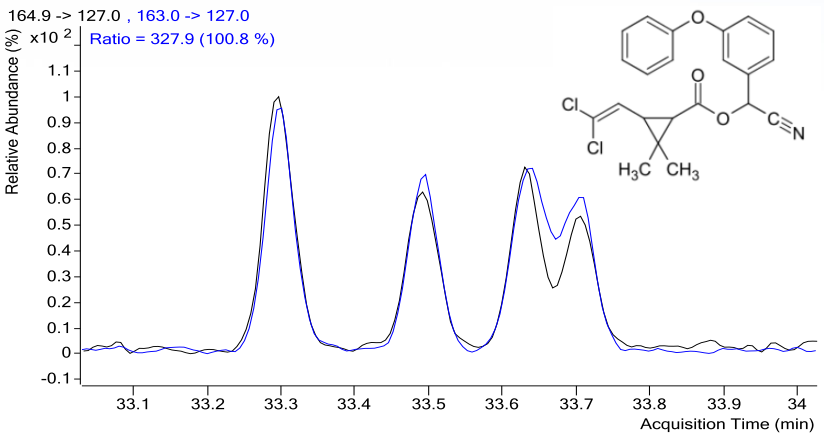


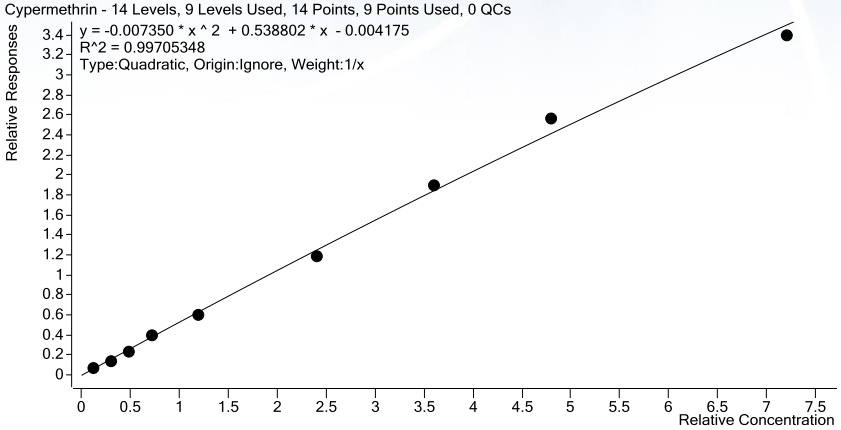
0.030 ng/L in mineral water, LOQ 0.030 ng/L

3 pg on column (100 mL sample, assumption 100% recovery)

Required LOQ 0.75 ng/L (inland surface water)

Cypermethrine – Ground Water





0.12 ng/L in ground water, LOQ 0.12 ng/L

12 pg on column (100 mL sample, assumption 100% recovery)

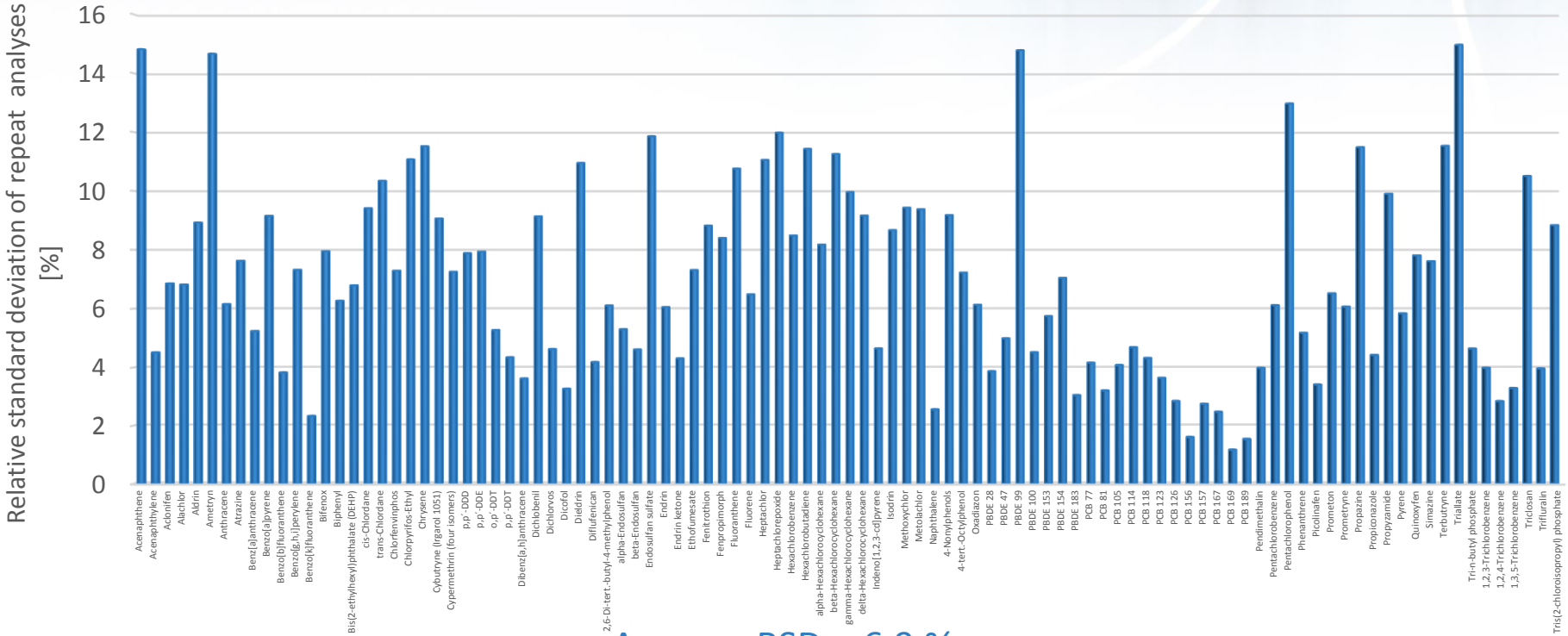
Required LOQ 0.024 ng/L (inland surface water)

Precision of Repeat Analyses [%]

GERSTEL

Agilent
Trusted Answers

Spiked Mineral Water near LOQ (n=6)



Average RSD = 6.9 %

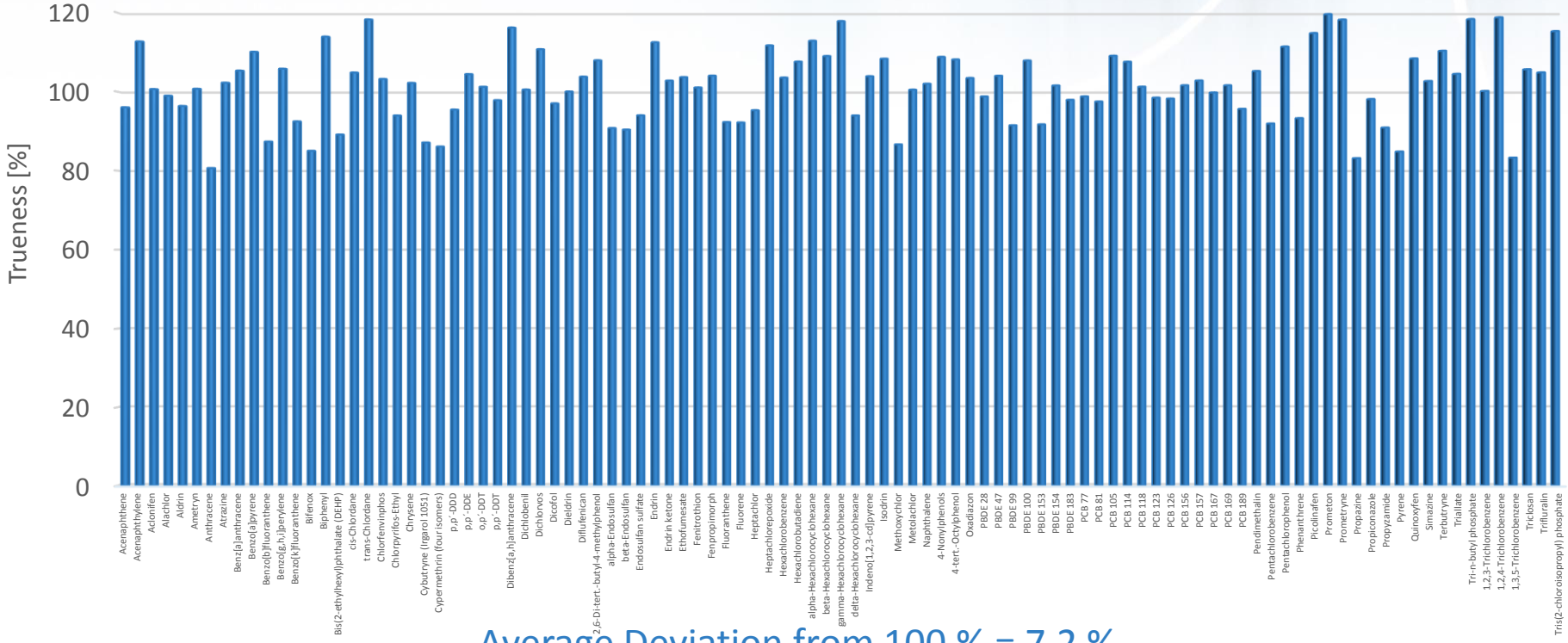
Trueness

GERSTEL

Agilent

Trusted Answers

Spiked Mineral Water near LOQ (n=6)



Average Deviation from 100 % = 7.2 %

Particle Load of Surface Water Samples*

- Data on suspended particulate matter (SPM) in characteristic French water samples, presented at CEN/TC 230 meeting – Paris, March 14-15, 2019
- 94% of water samples have a SPM load < 50 mg/L (with a 84% majority at SPM < 25 mg/L). Less than 1% of the samples had an SPM > 200 mg/L
- Effectiveness of LLE or SPE for extraction of analytes from SPM normally not proven/validated

* Personal communication Frank David, RIC

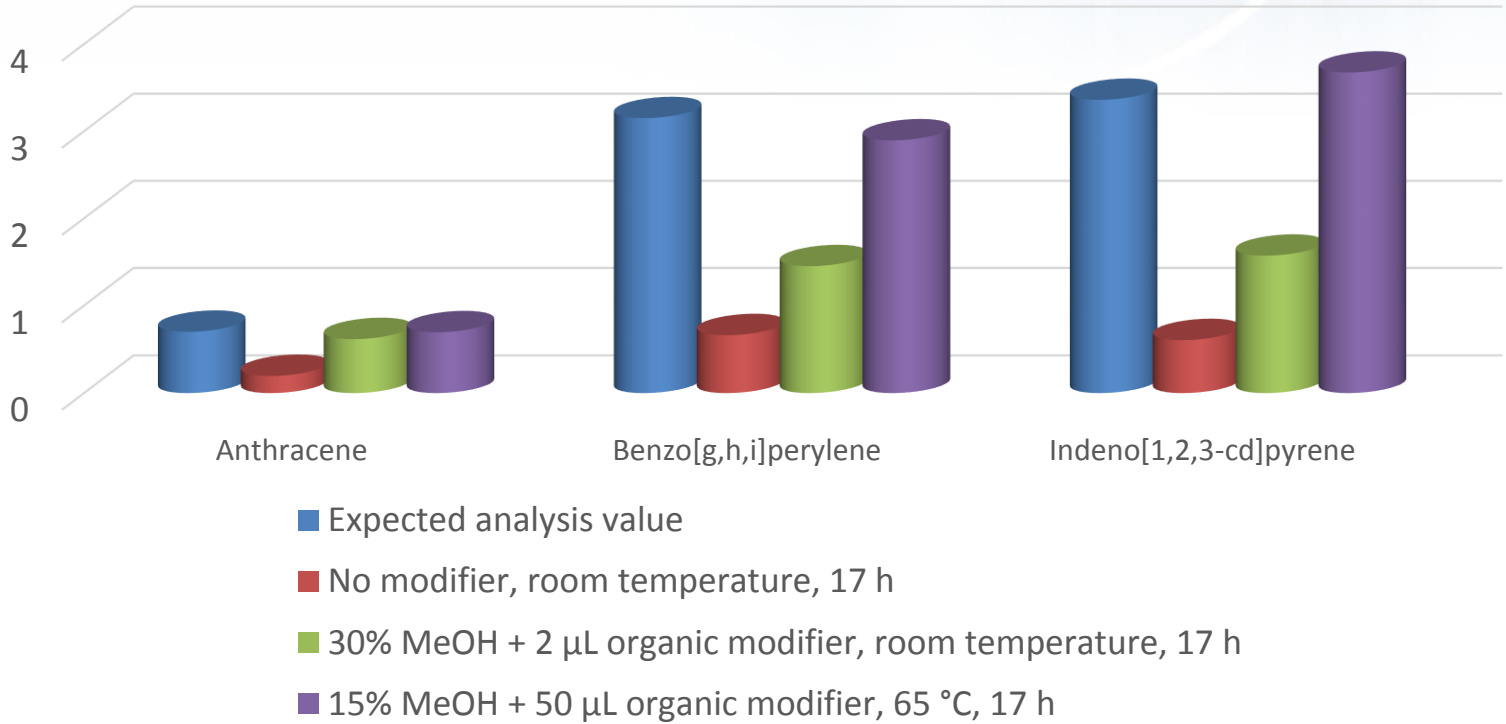
Extraction of Particle adsorbed Analytes

5, 10 or 15 mg
WEPAL SETOC 745
reference sediment

100 mL tap water
(50, 100 or 150 mg particles/L)
+ internal standard

Twister extraction under heating
TDU-GC-MS/MS
-> Analysis results

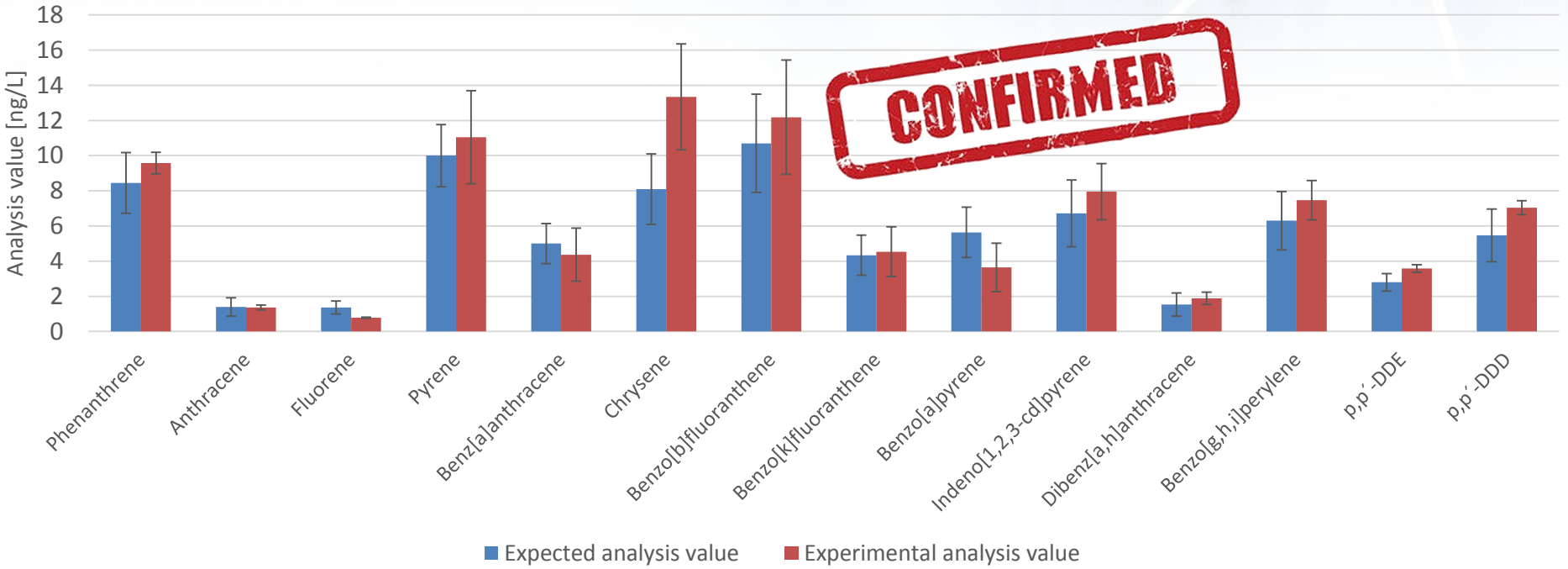
Extraction Parameters – “Sequential SBSE”



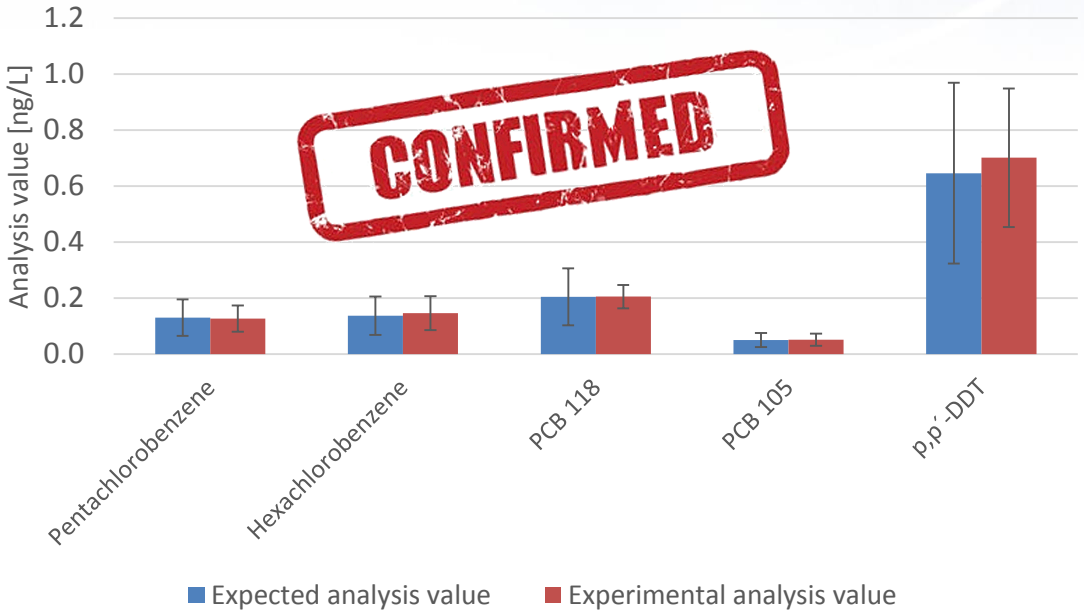
Extraction of Particle adsorbed Analytes
10 mg Sediment in 100 mL Water (100 mg/L)

GERSTEL

Agilent
Trusted Answers



Extraction of Particle adsorbed Analytes 10 mg Sediment in 100 mL Water (100 mg/L)

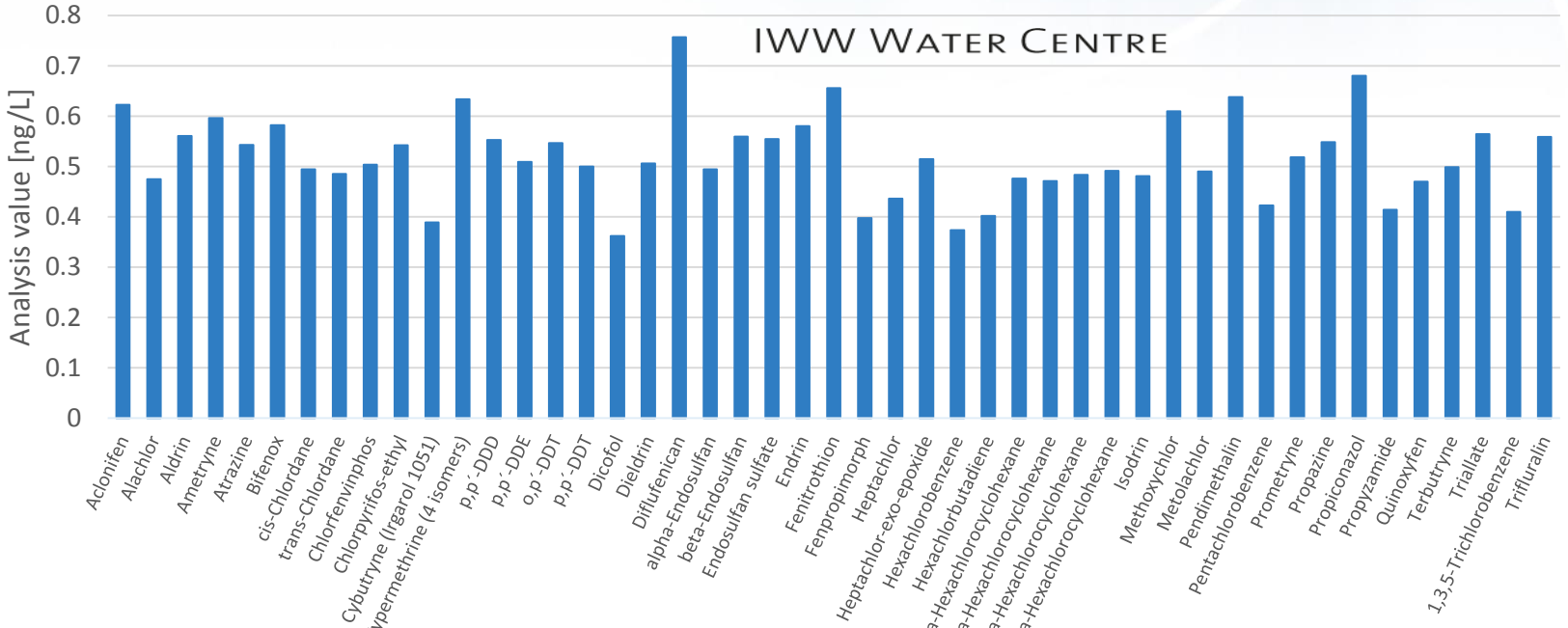


Externally spiked Ground Water Sample at 0.5 ng/L

GERSTEL

Agilent
Trusted Answers

IWW
IWW Water Centre



Analysis of real Water Samples Concentrations in ng/L

GERSTEL

Agilent

Trusted Answers

Channel	
Ametryne 3.4	Fluoranthene 0.73
Anthracene 0.28	alpha Hexachlorocyclohexane, 0.14
Atrazine 0.51	gamma Hexachlorocyclohexane 0.12
Benz[a]anthracene 0.21	Indeno[1,2,3-cd]pyrene 0.39
Benzo[a]pyrene 0.33	Metolachlor 8.2
Benzo[b]fluoranthene 0.33	Nonylphenol 11
Benzo[g,h,i]perylene 0.20	Propiconazol 0.57
Benzo[k]fluoranthene 0.20	Propyzamide 19
trans-Chlordane 0.035	Pyrene 0.53
Chrysene 0.40	Tebutryne 0.22
Cybutryne 1.1	Tris(2-chloroisopropyl) phosphate (TCPP) 52
Diflufenican 2.6	23 compounds >LOQ

Sewage Treatment Plant Effluent			
Acenaphthylene 0.22	Dibenz[a,h]anthracene 0.20	4-Nonylphenols 199	Pyrene 2.5
Alachlor 0.46	Dieldrin 0.084	4-Octylphenol 11	Terbutryne 6.1
Anthracene 0.42	Diflufenican 0.39	PBDE 47 0.098	Triallate 0.16
Atrazine 1.6	2,6-Di-tert.-butyl-4-methylphenol 6.4	PBDE 99 0.23	Triclosan 9.9
Benz[a]anthracene 1.5	alpha Endosulfan 0.24	PBDE 100 0.046	Tri-n-butylphosphate 39
Benzo[a]pyrene 1.9	Ethofumesate 0.32	PBDE 154 0.031	Tris(2-chloroisopropyl) phosphate (TCPP) >300
Benzo[b]fluoranthene 2.1	Fluoranthene 2.3	PCB 118 0.021	42 compounds >LOQ
Benzo[g,h,i]perylene 2.0	alpha Hexachlorocyclohexane 0.071	Pendimethalin 0.36	
Benzo[k]fluoranthene 1.1	beta Hexachlorocyclohexane, 0.31	Pentachlorobenzene 0.099	
Chlorpyrifos-ethyl 0.23	gamma Hexachlorocyclohexane, 1.4	Propazine 0.11	
Chrysene 1.9	Indeno[1,2,3-cd]pyrene 2.6	Propiconazol 6.1	
Cybutryne 0.28	Metolachlor 3.8	Propyzamide 2.7	

Tap Water
Anthracene 0.069
trans-Chlordane 0.038
alpha Hexachlorocyclohexane 0.065
beta Hexachlorocyclohexane 0.15
gamma Hexachlorocyclohexane 0.056
4-Nonylphenols 5.9
4-Octylphenol 2.3
7 compounds >LOQ

Conclusions

- Employing the Twister with Agilent 7010 (HES) is useful for EU-WFD guided water analysis
- LOQ of analytes mainly in the range of two to three digit pg/L
- Analysis method works for around 100 relevant compounds, further can be added
- Required LOQs for inland surface water are achieved for all chosen analytes except heptachlor, heptachlor-epoxide, cypermethrine
- Extraction of particle adsorbed compounds is feasible and was confirmed for a reference sediment
- Ready to use GERSTEL “Sample Prep Solution” with defined hardware and method, manual, validation data etc.
- Many laboratories in Spain successfully use Twister for EU-WFD work, also labs in Germany (state lab in Augsburg, Bavaria and state lab in Neumünster, Schleswig Holstein) and other European countries