A preliminary survey of PFAS in farmed marine shellfish in Greece. Do PFAS pose a threat to marine biota and human health?

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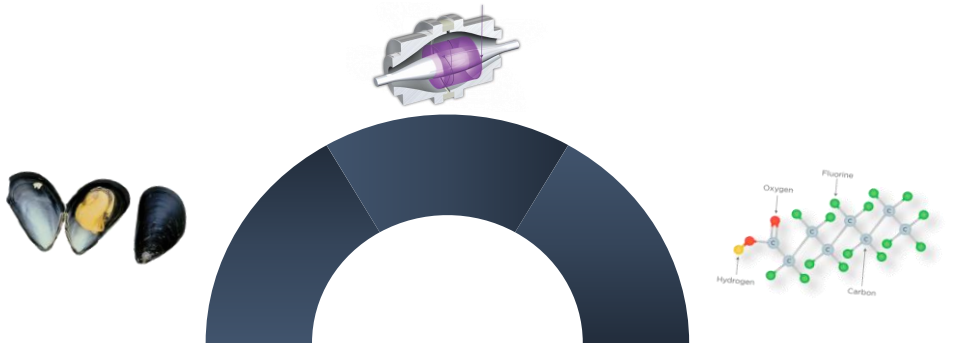
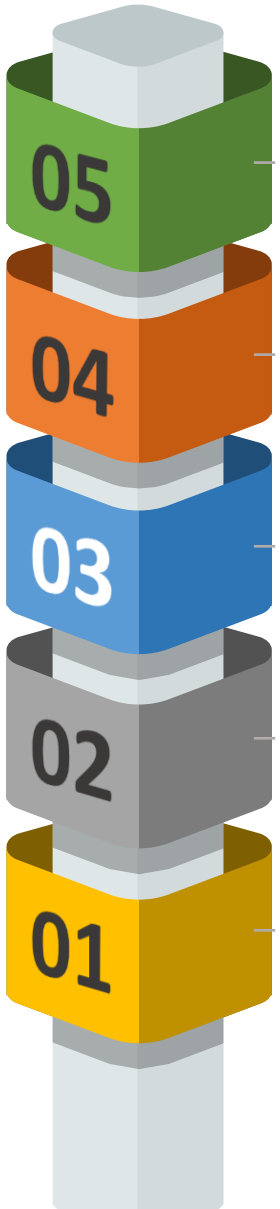
2 Centre for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 10th km Thessaloniki-Thermi Rd, GR 57001, Greece

ISO Fd Food ERA Chair Safety Quality Traceability



Outline of presentation



05 Conclusions

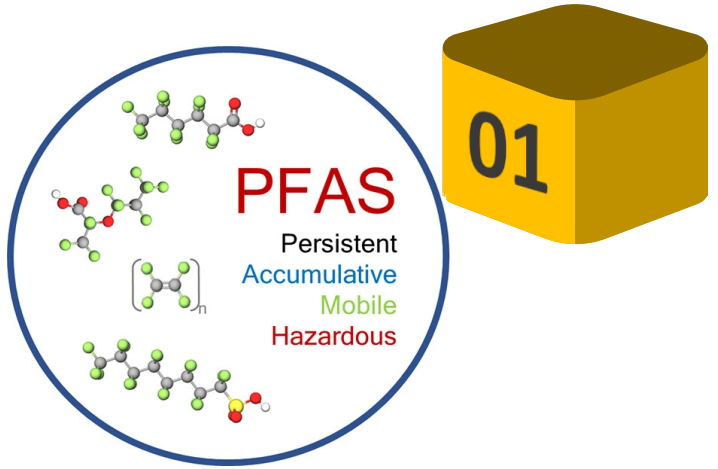
04 Evaluated pretreatment protocols & analysis

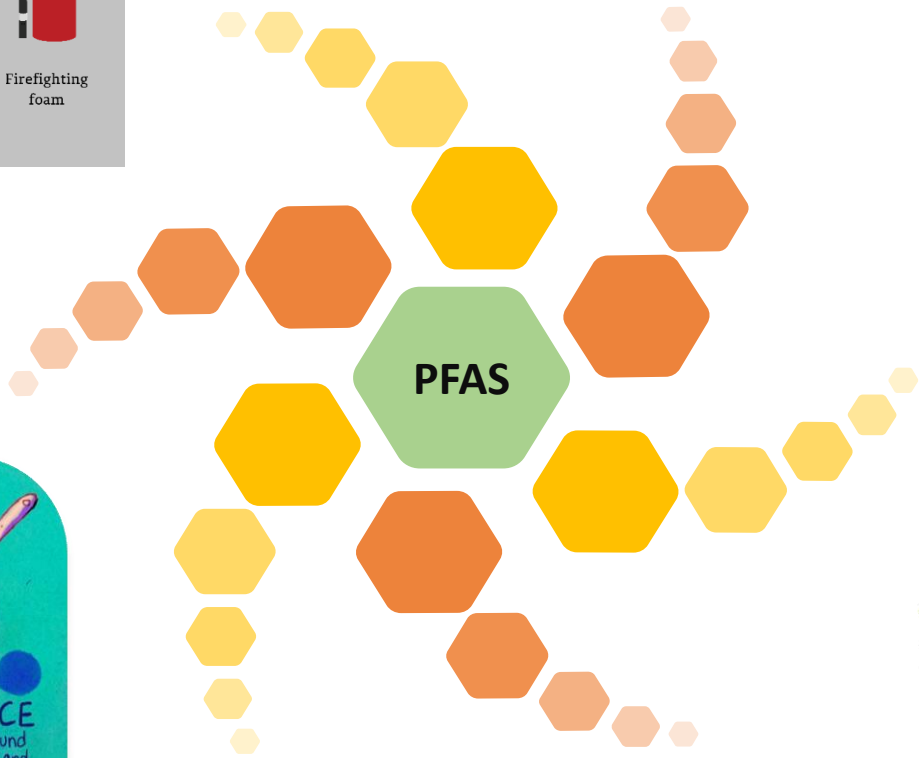
03 Sampling points

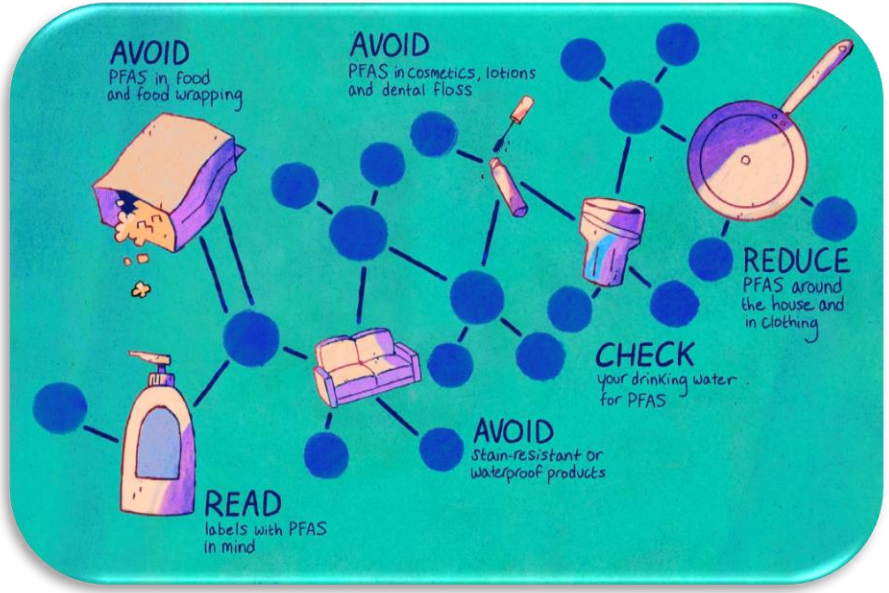
02 HRMS; a cutting edge technology

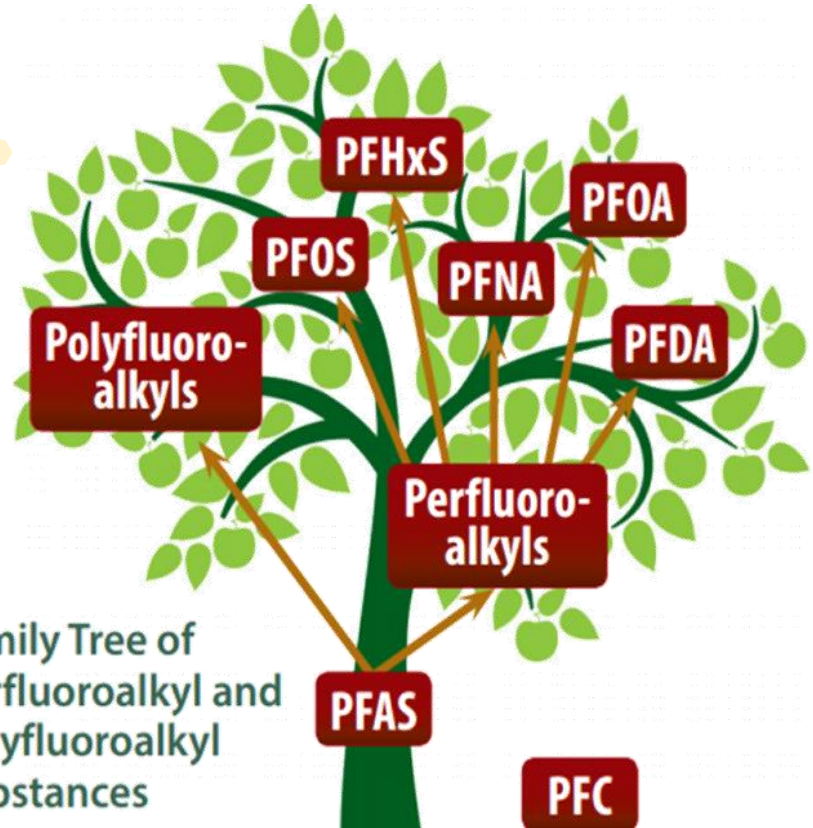
01 PFAS; an emerging concern

PFAS; an emerging concern

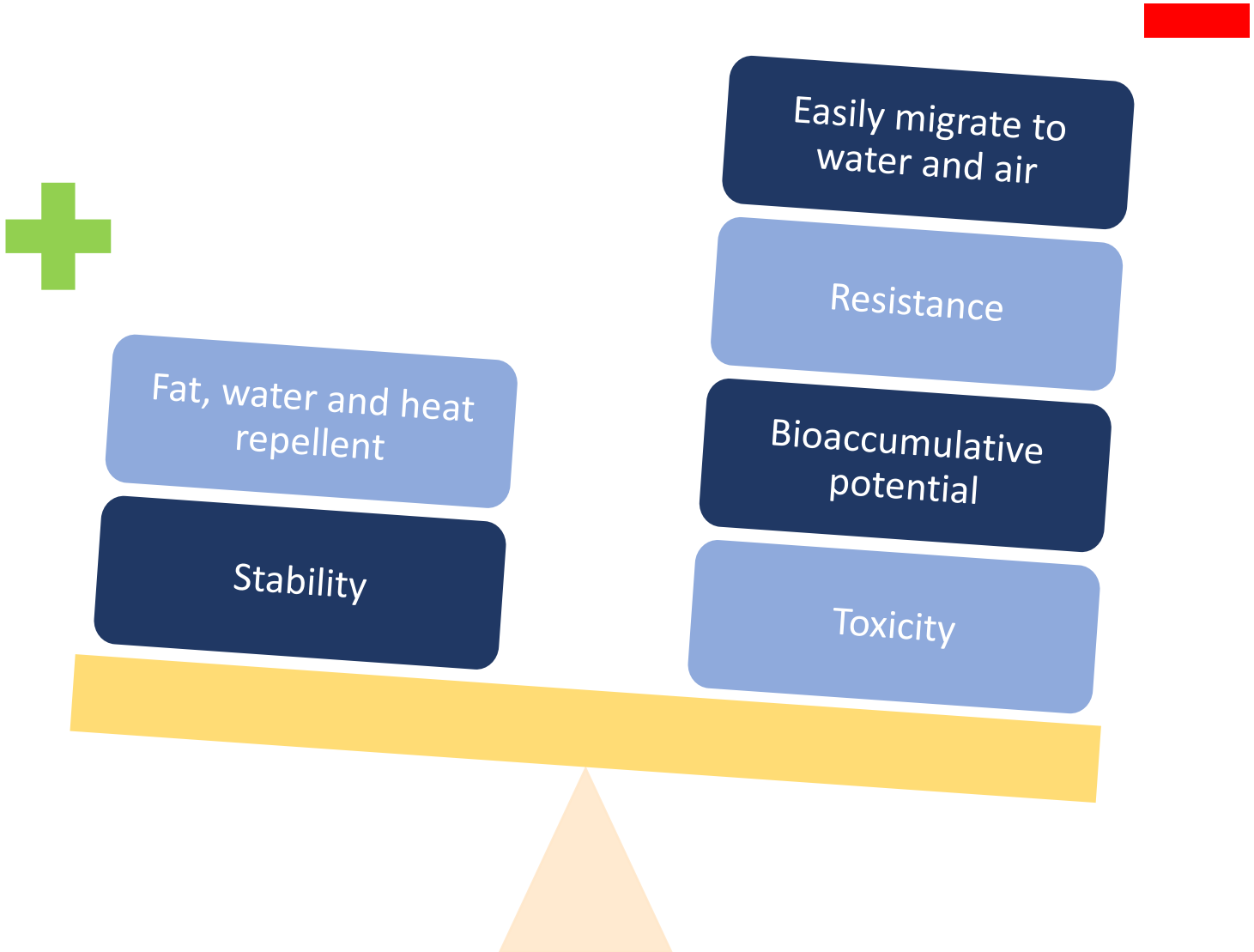








PFAS; an emerging concern



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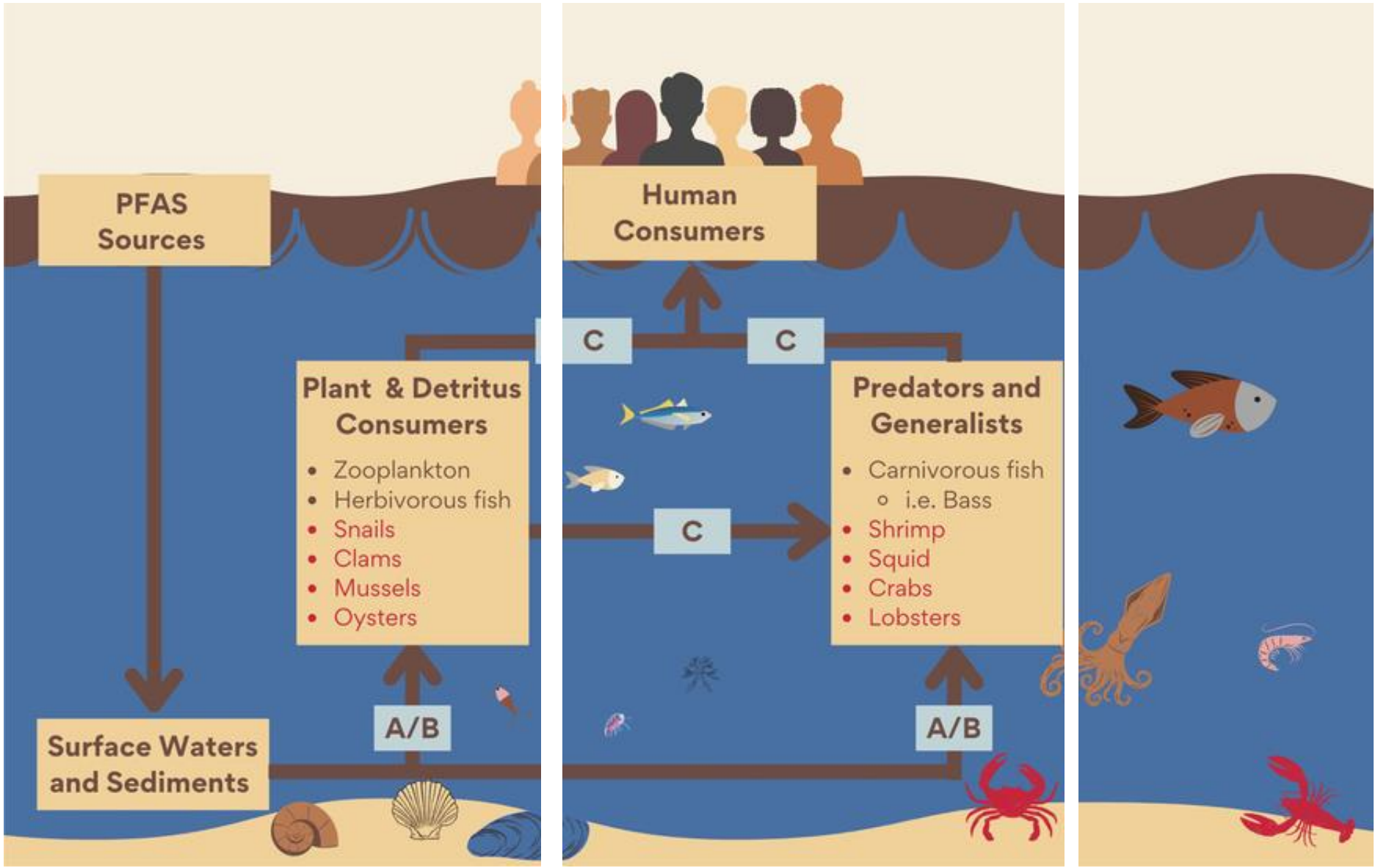
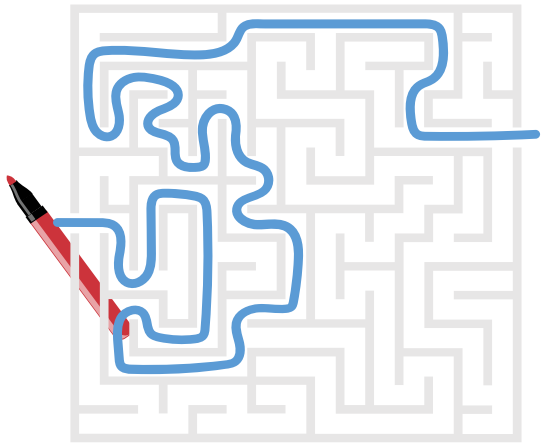
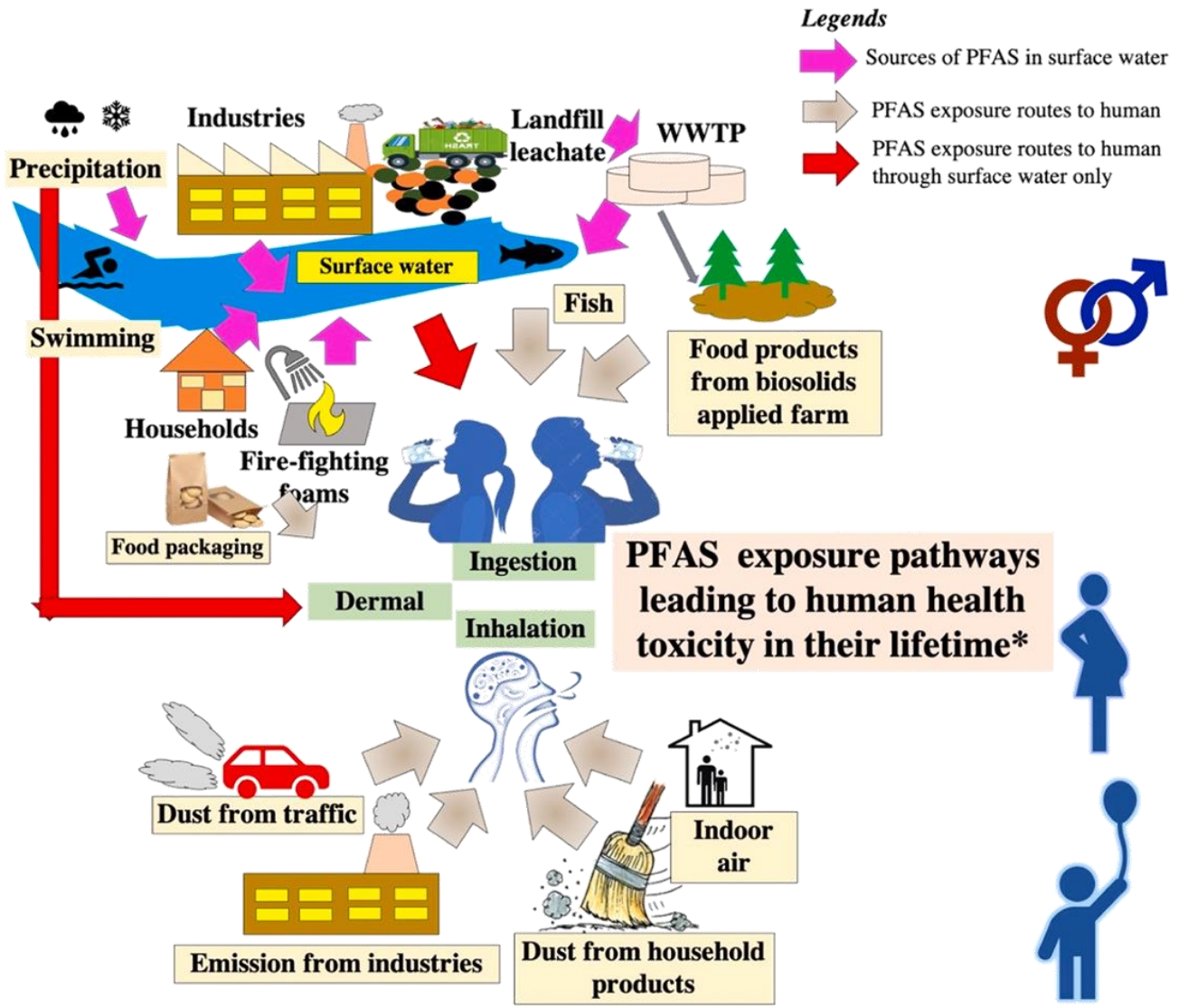




PFAS; an emerging concern

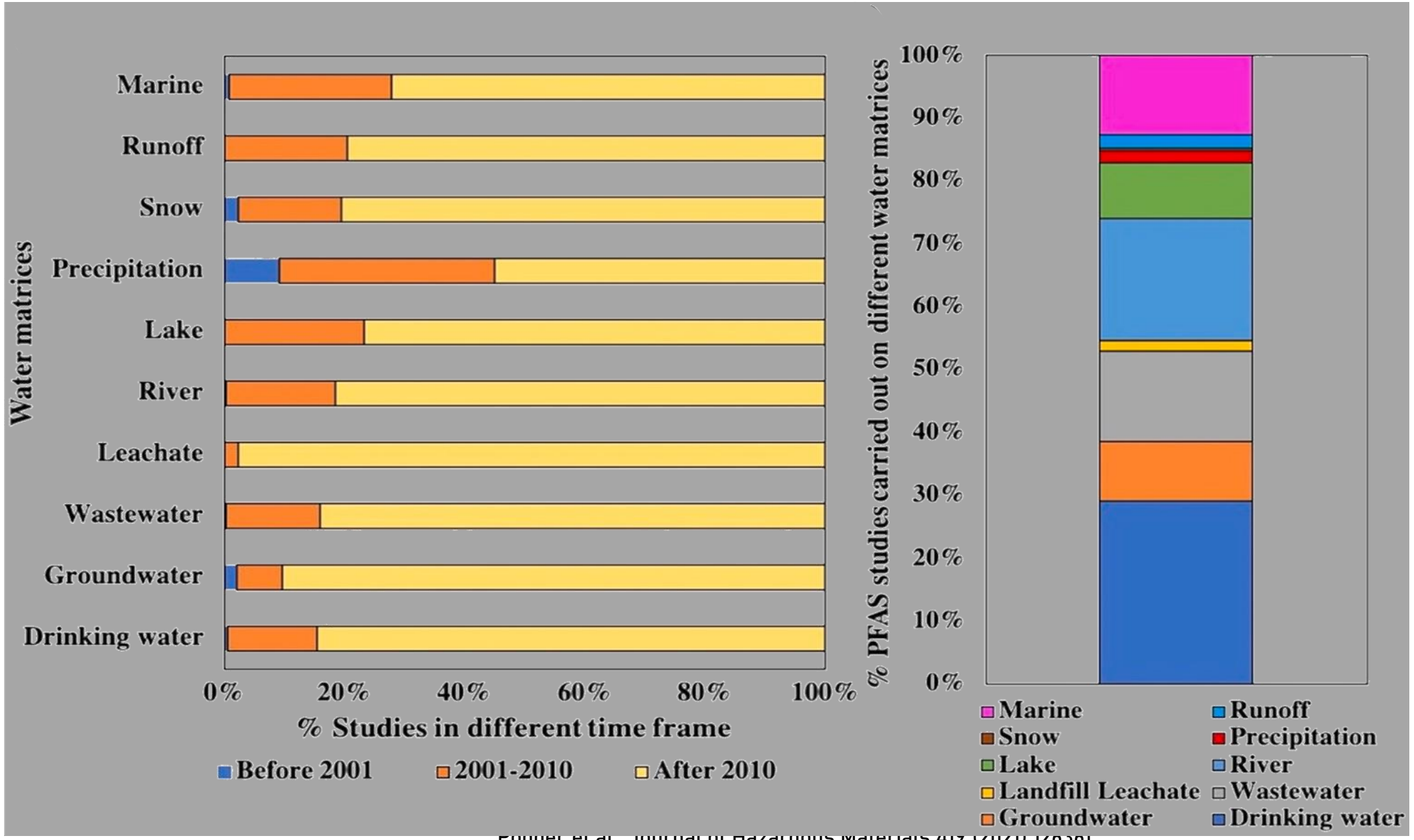


- Altered metabolism
- Altered liver functions
- Cancer
- Chronic kidney damages
- Cardiovascular diseases
- Diabetes
- Increased cholesterol levels
- Inflammatory bowel diseases
- Lower chance of getting pregnant
- Osteoarthritis
- Reduced immune system
- Thyroid diseases

- Hormonal imbalance
- Delayed mammary gland development
- Reduced fetal growth
- Pregnancy induced hypertension or pre-eclampsia
- Increased miscarriage risk
- Preterm birth

- Low birth weight
- Childhood obesity
- Emotional and behavioral disorders
- Obesity
- Early puberty

Podder et al., Journal of Hazardous Materials 419 (2021) 126361



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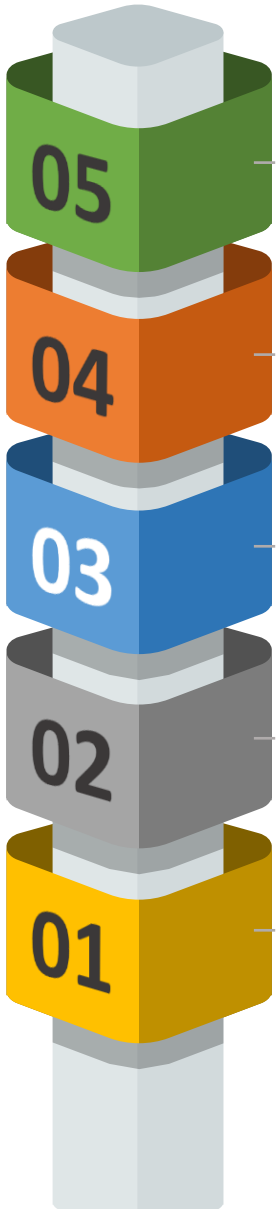
Outline of presentation



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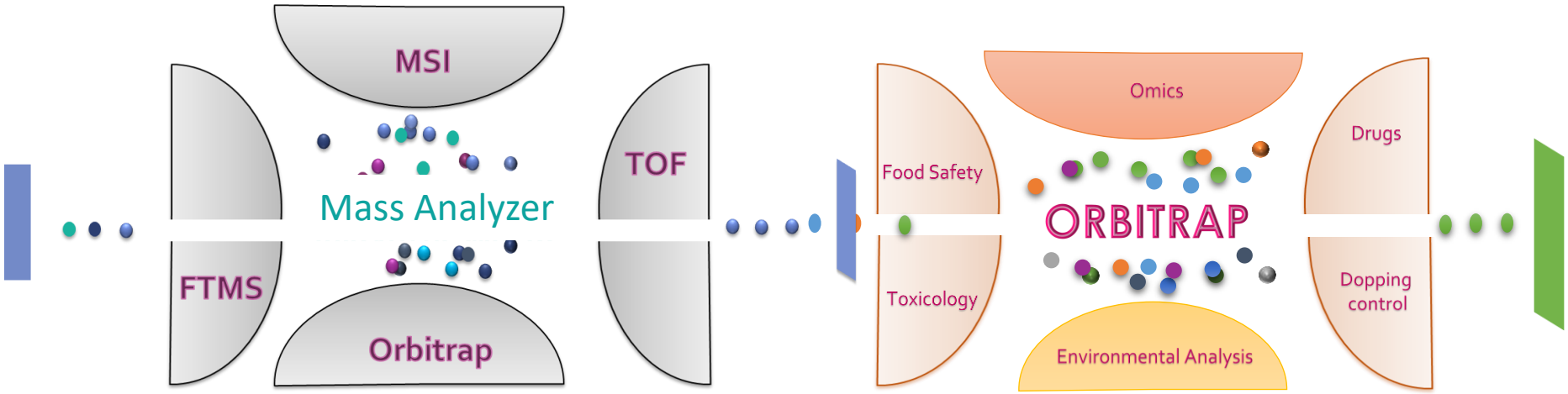
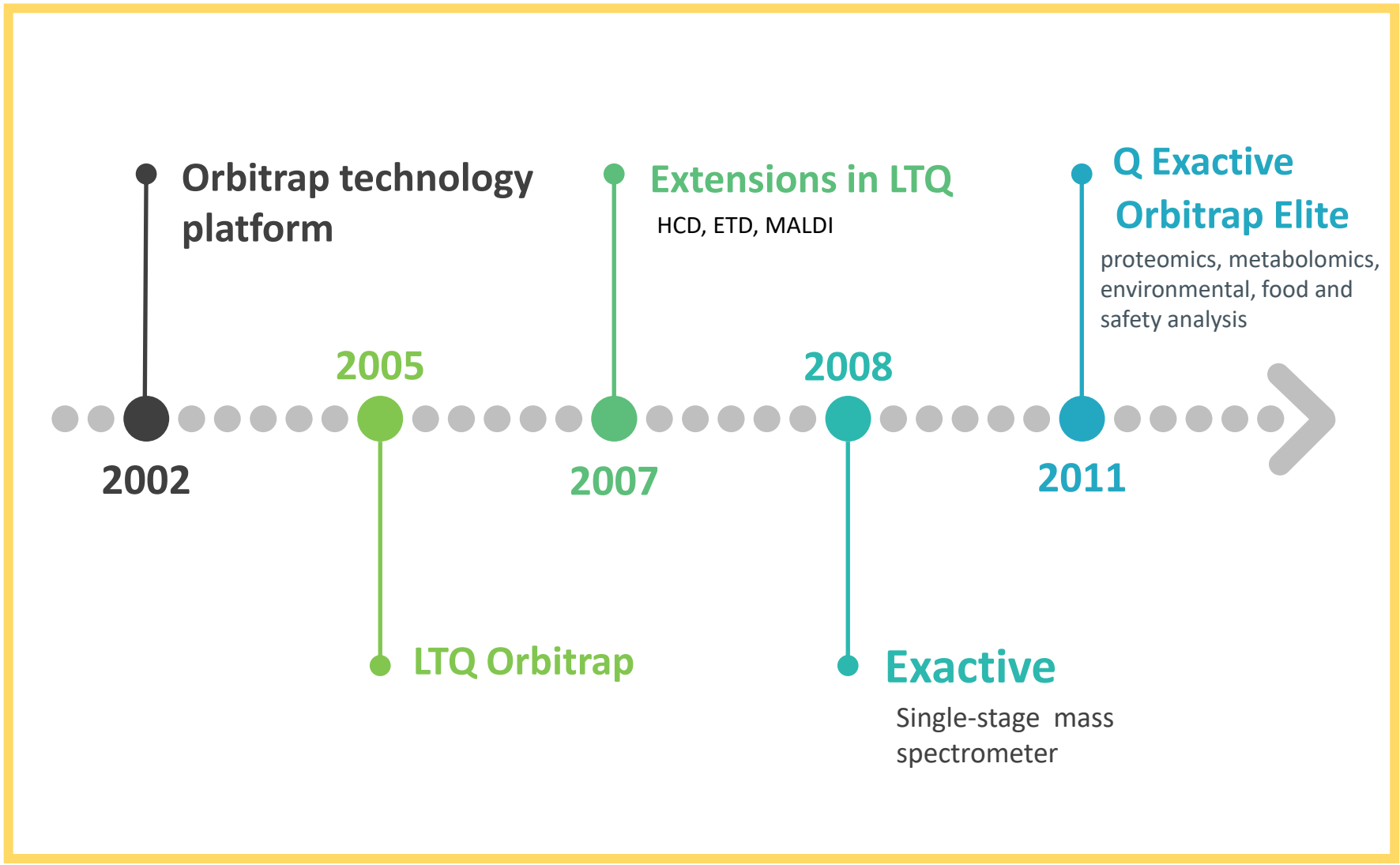
Orbitrap Mass Analyzer

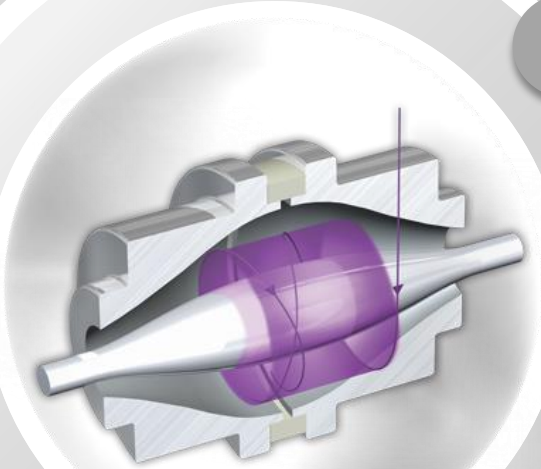


Orbitrap Mass Analyzer



Orbitrap Mass Analyzer

02

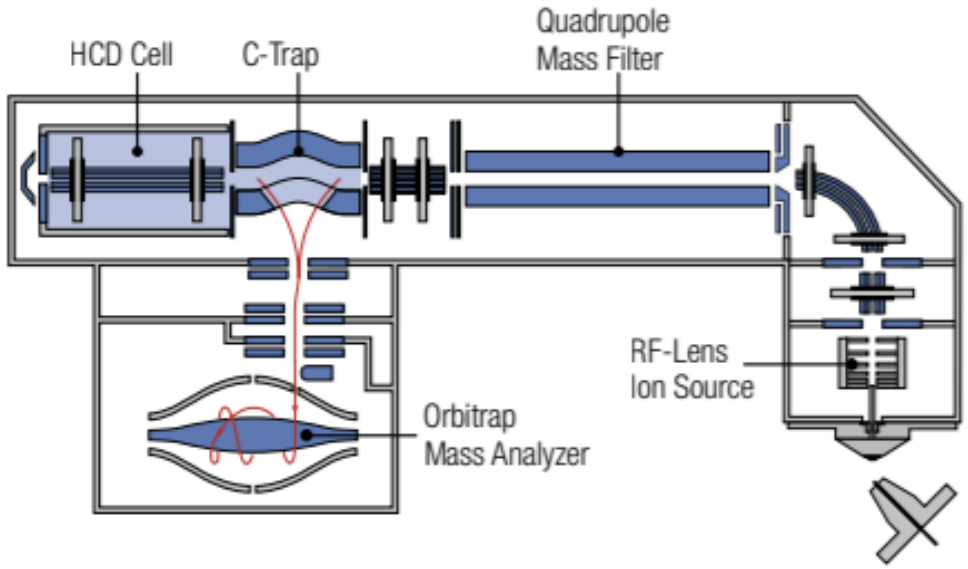


1. Mass range *m/z* 50-2000
2. Resolution: 70,000 (Min: 7500, Max: >100000 (*m/z* 400)
3. Mass accuracy <5 ppm
4. Dynamic range>4000 per scan
5. Sensitivity (sub-ppt)
6. MS2 (data dependent, data independent, SIM, PRM, AIF)

Orbitrap Mass Analyzer

02

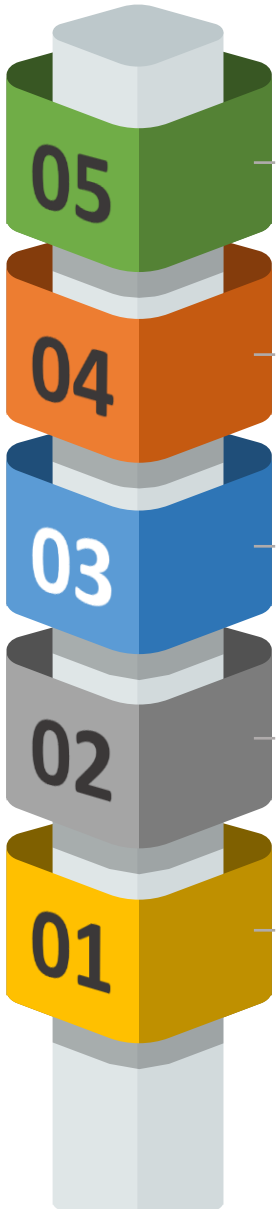
Q Exactive Focus Orbitrap



Q Exactive Focus schematics diagram

- Scan speed up to 12 Hz
- Resolving power up to 70,000 (FWHM) at m/z 200
- Routine sub ppm mass accuracy
- Linear Dynamic Range up to 6 orders of magnitude
- Multiple approaches for data acquisition (SIM, PRM, FS-ddMS or DIA)
- Polarity switching for maximum compound coverage
- HCD

Outline of presentation



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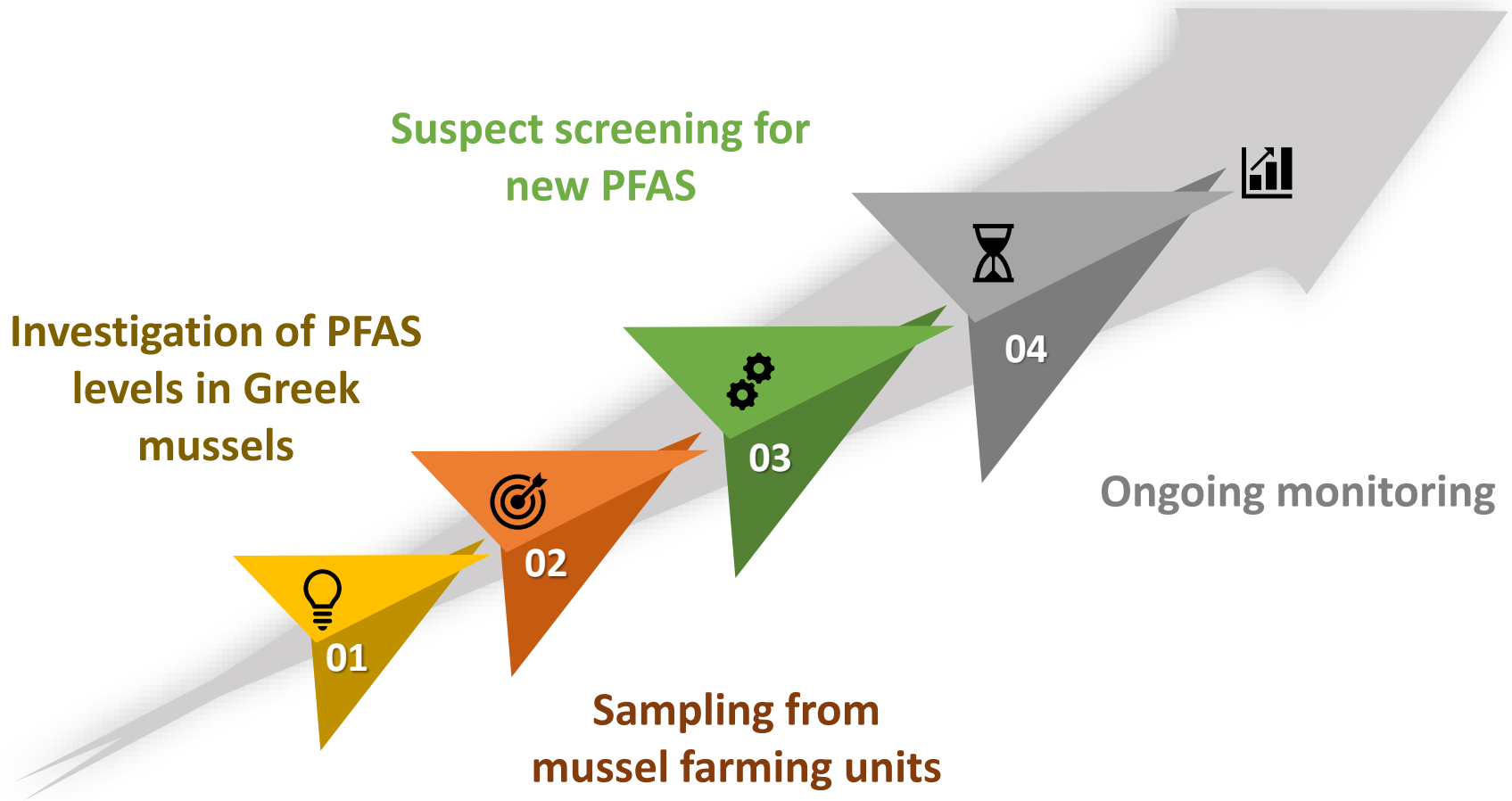
Aim of the study

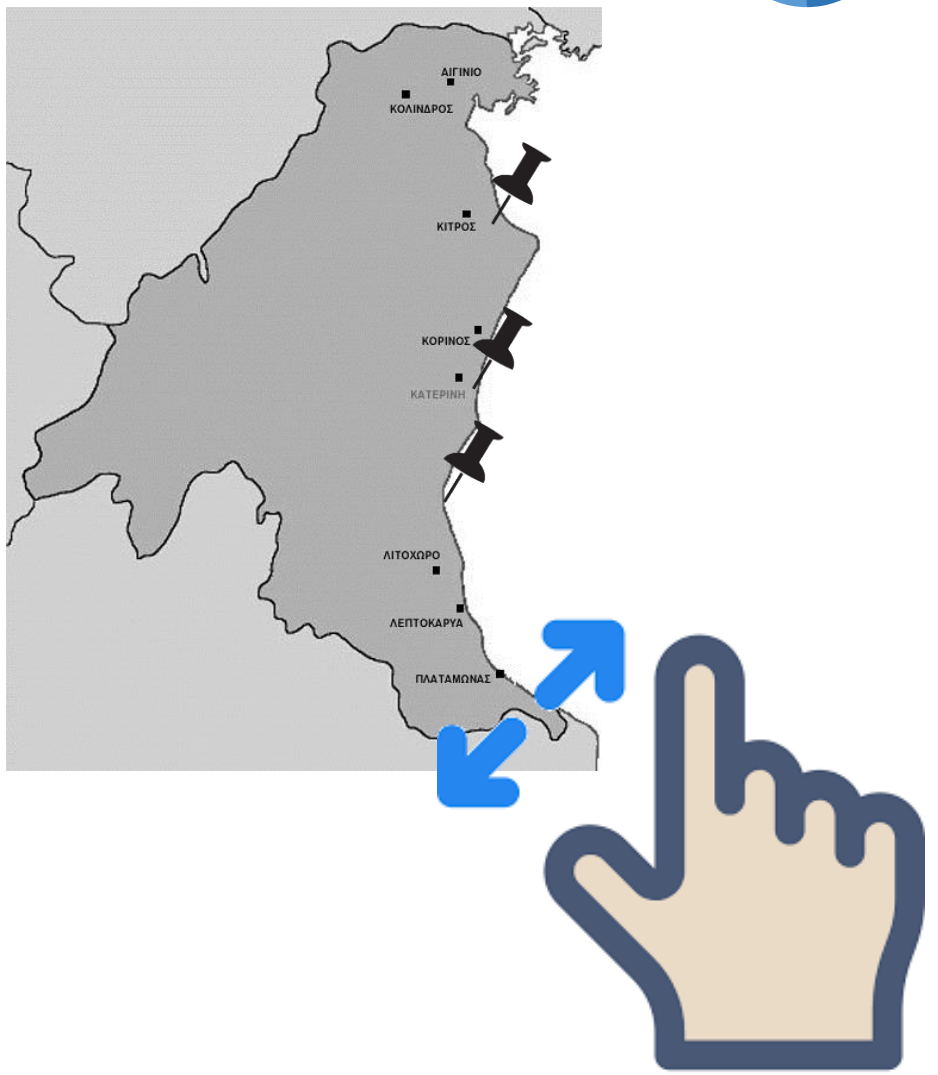


Mussel farming in Greece

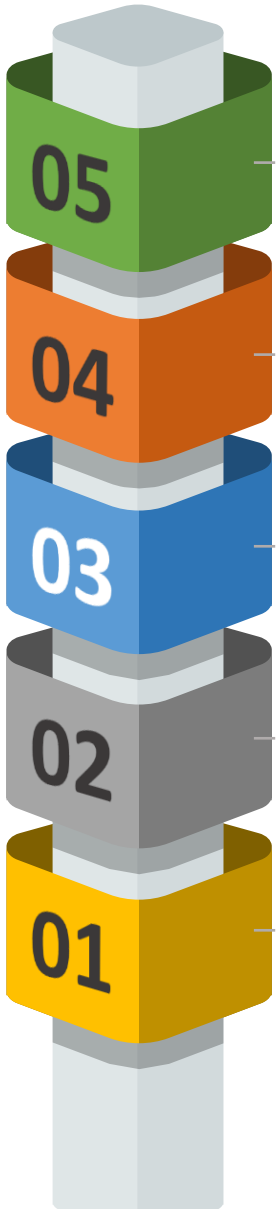
03

- Located in the North and South of Greece
- Main greek mussel farming units are located in the protected region of Axios-Loudias-Aliakmonas river Delta
- **Thermaikos gulf:** cultivated mussels reaching 80% of the national production

Sampling points



Outline of presentation



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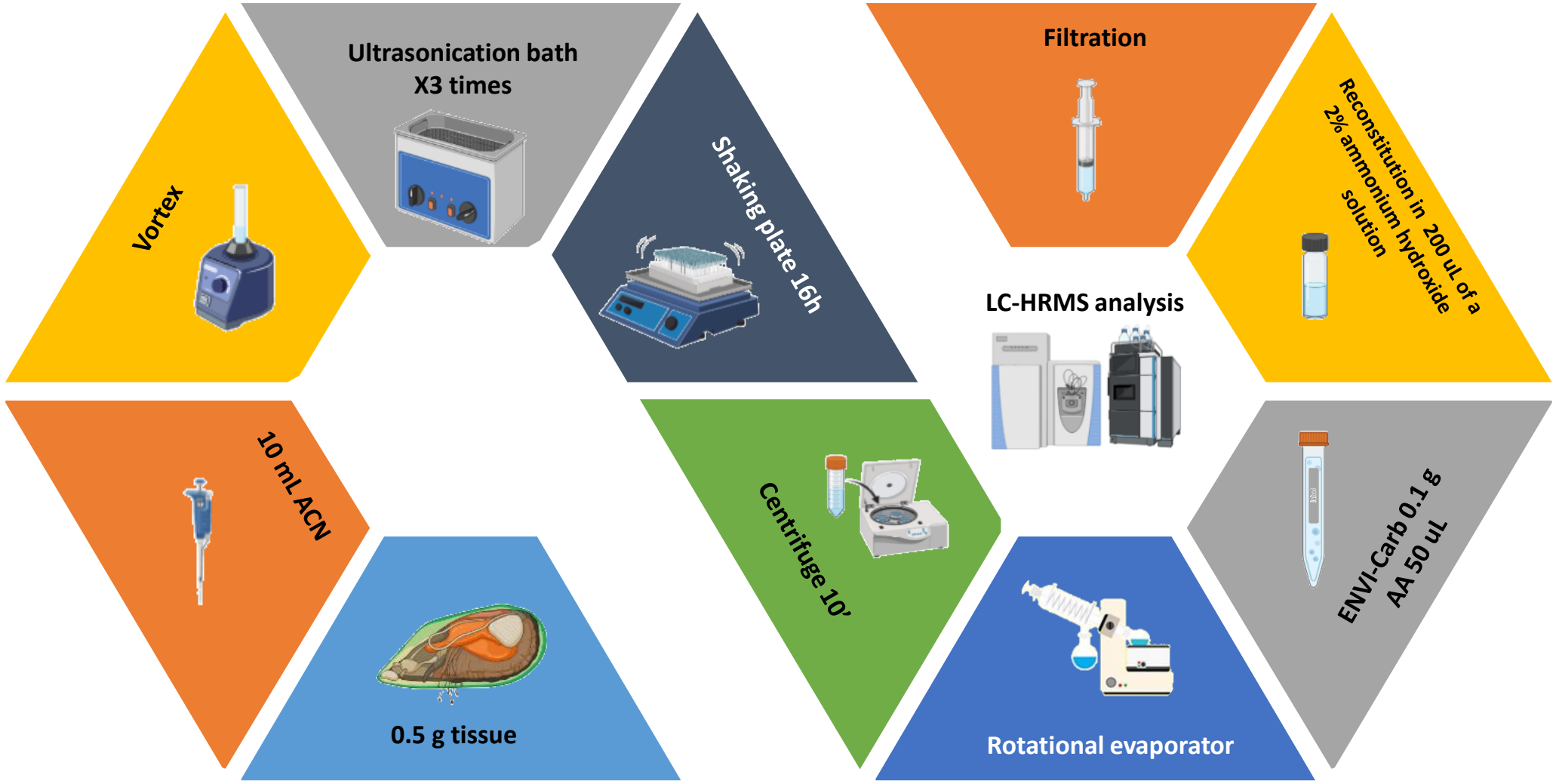
Evaluated Protocols

04

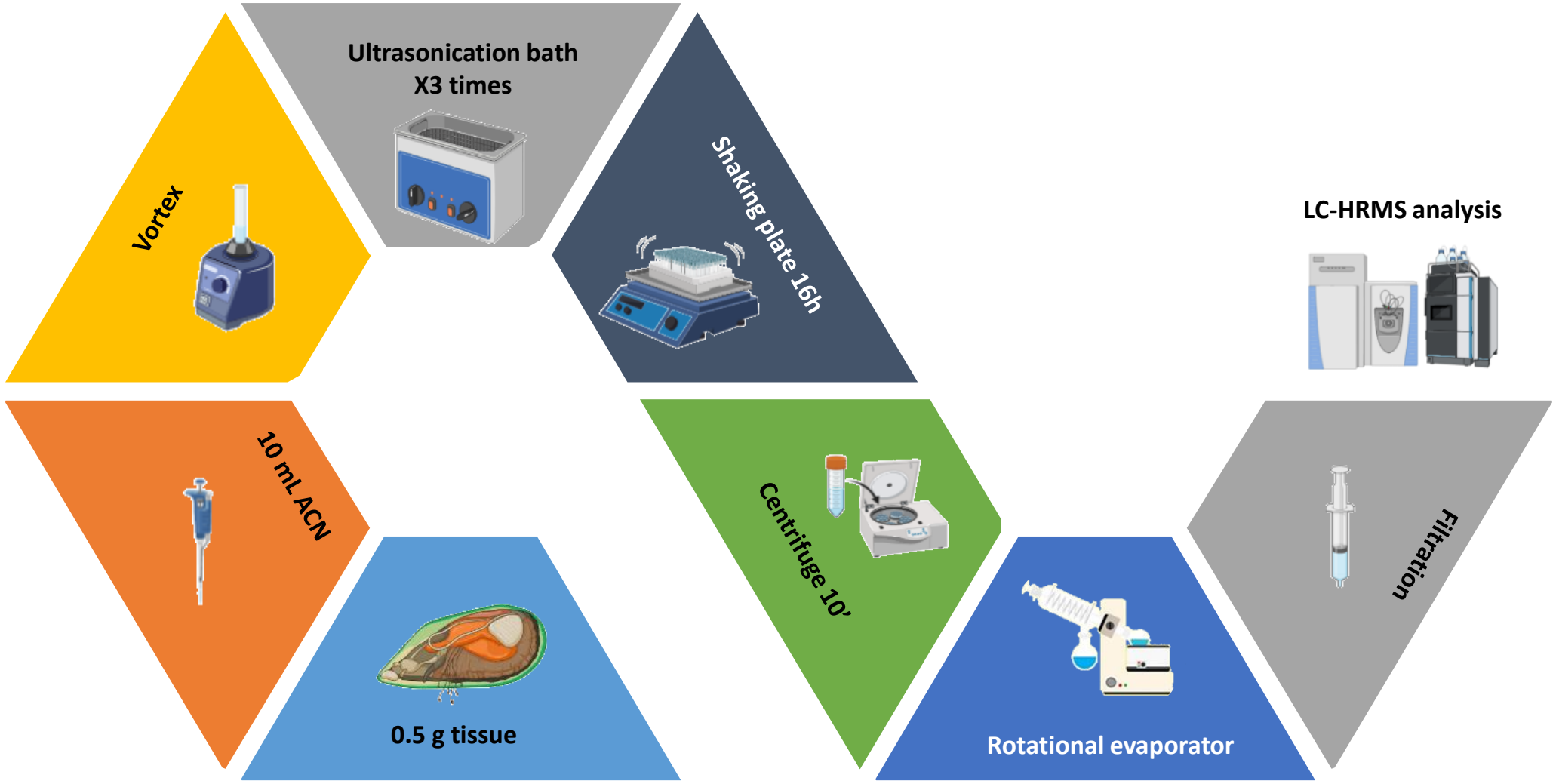
Protocol 1



Evaluated Protocols

04

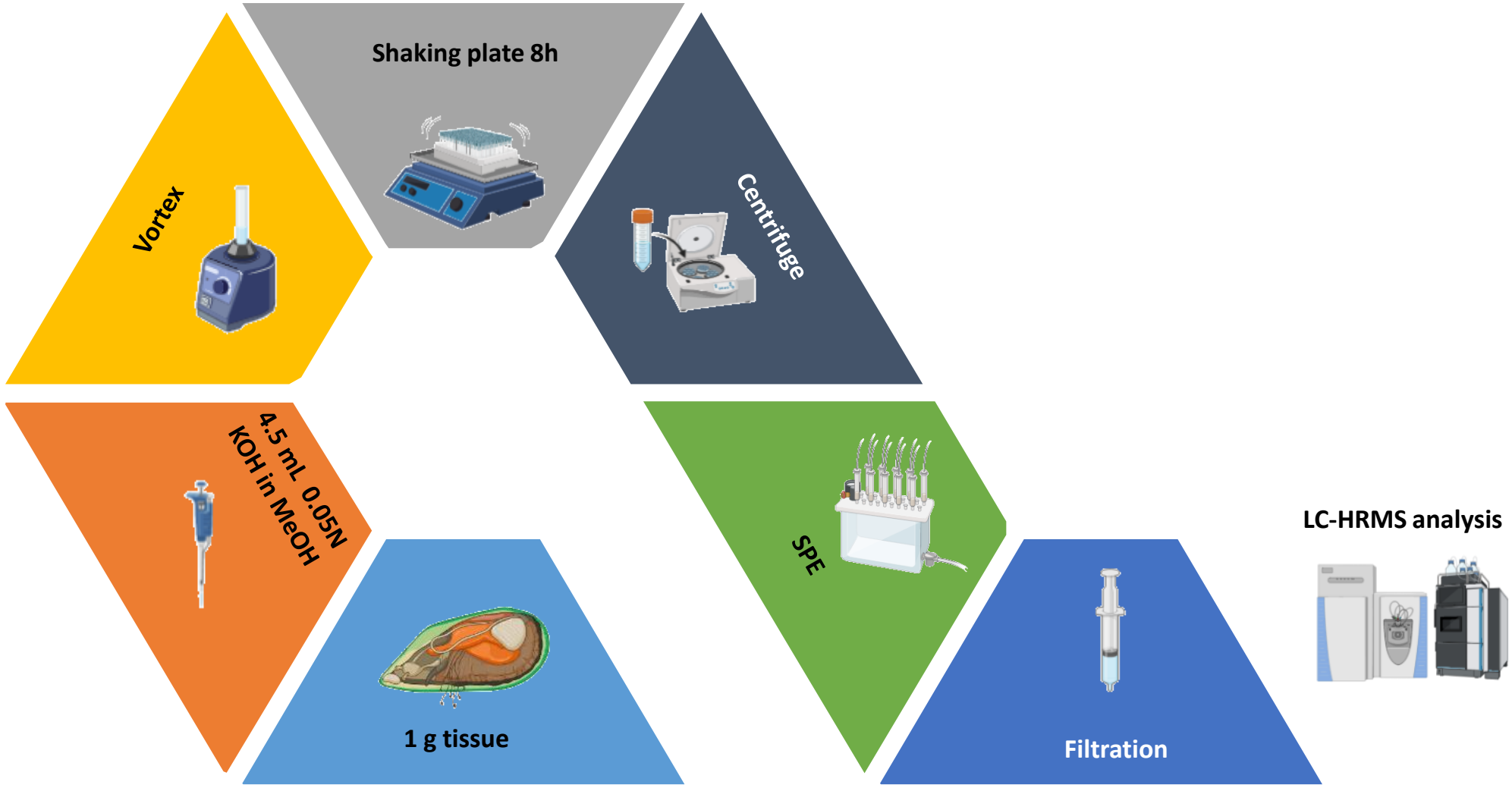
Protocol 2



Evaluated Protocols

04

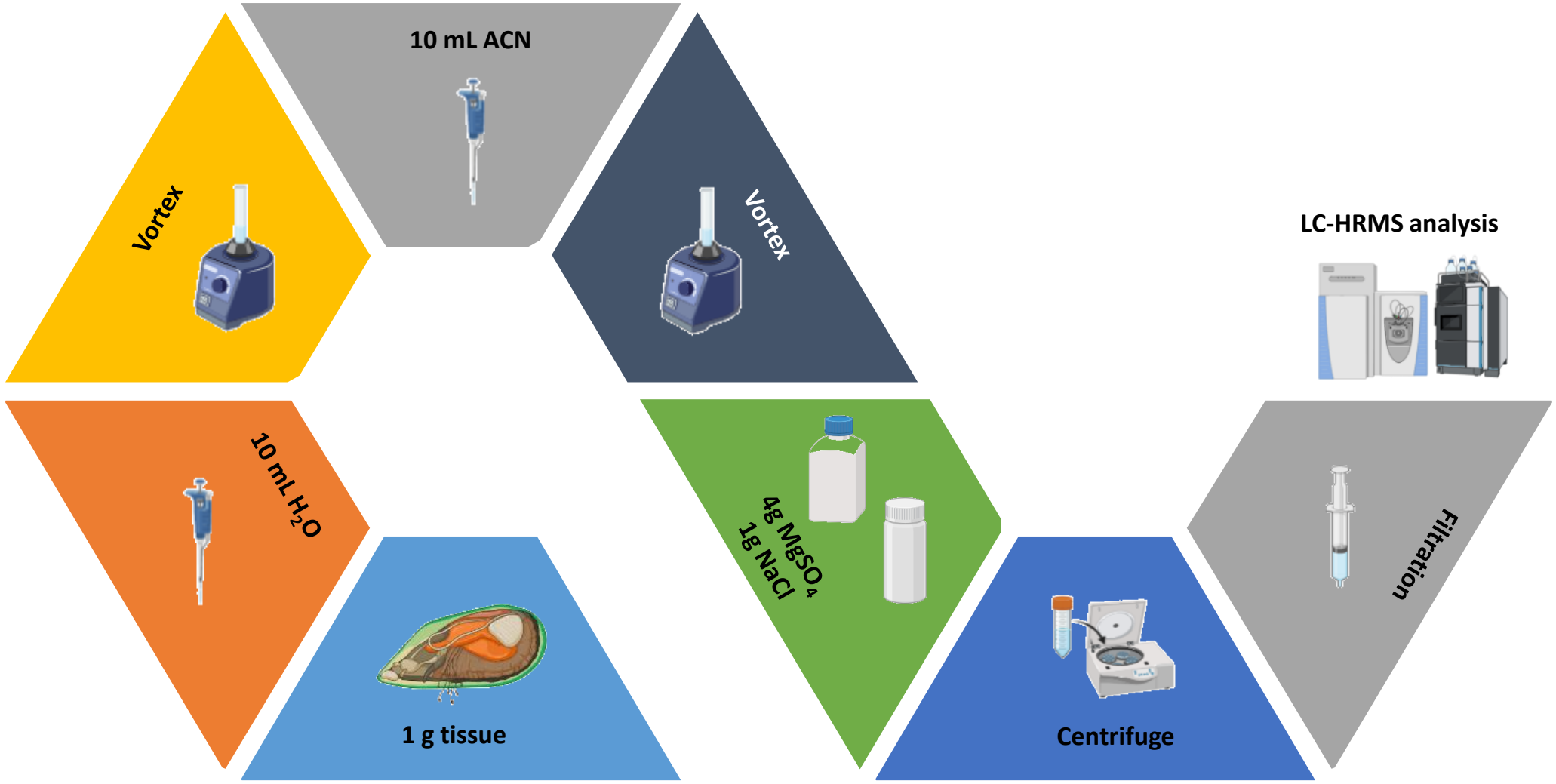
Protocol 3



Evaluated Protocols

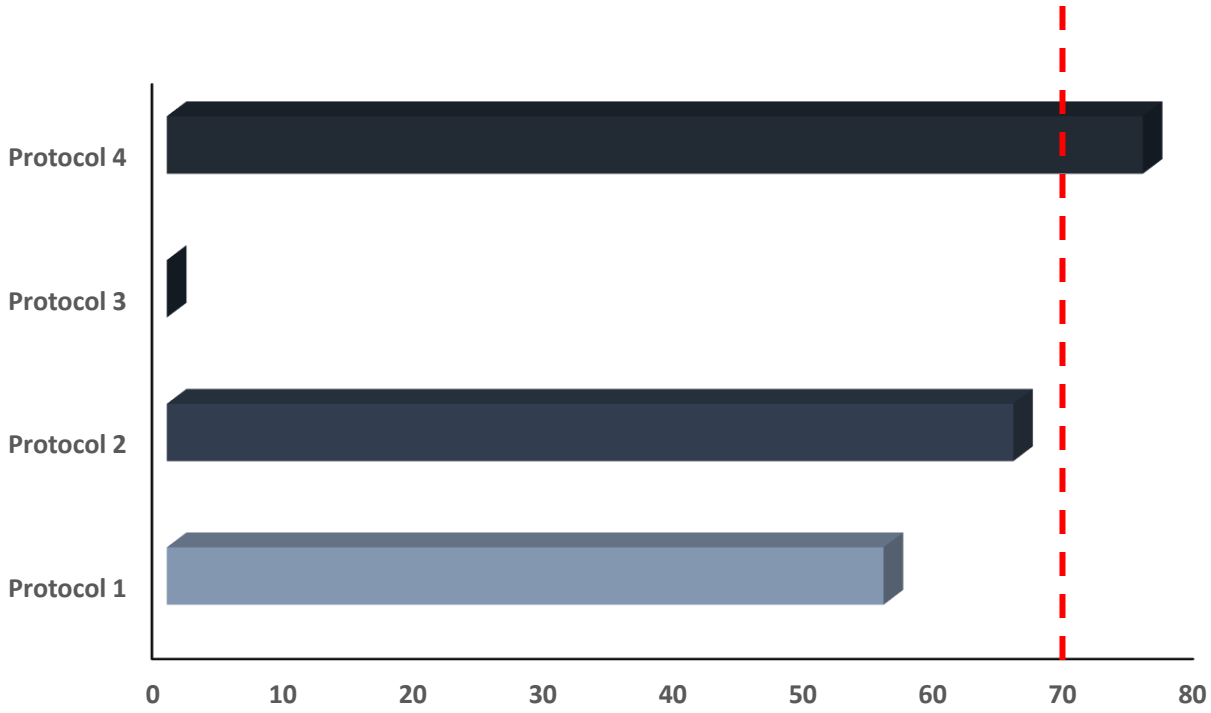
04

Protocol 4



Evaluated Protocols

- Protocols I, II, III, IV were evaluated in terms of recoveries



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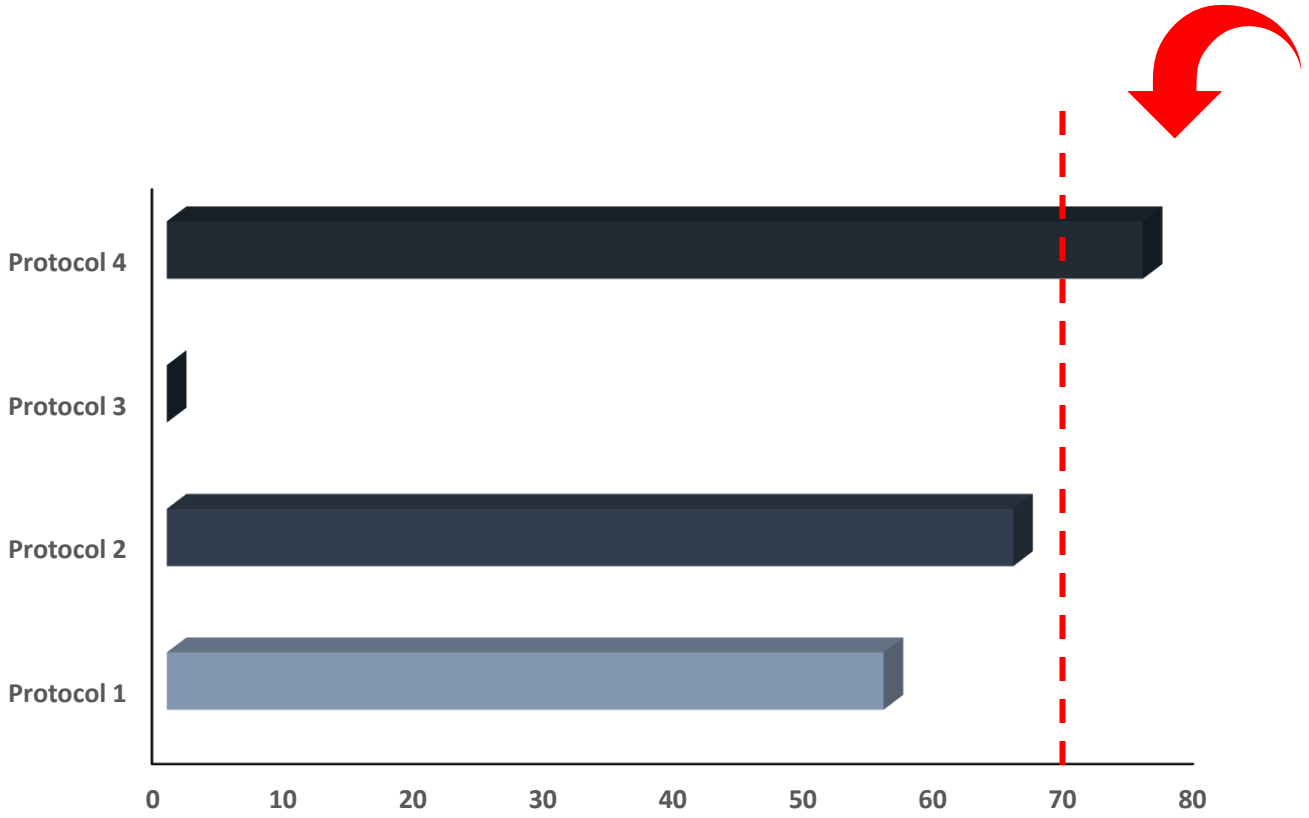

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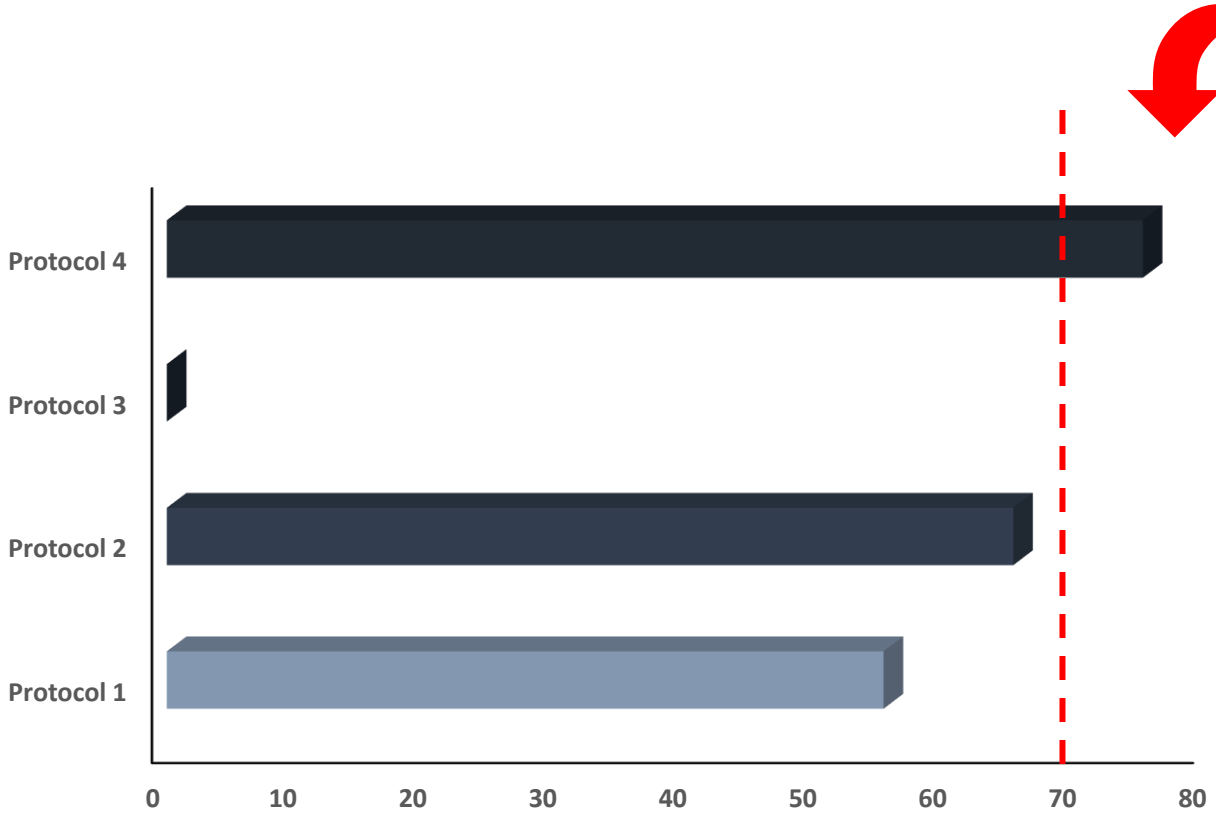
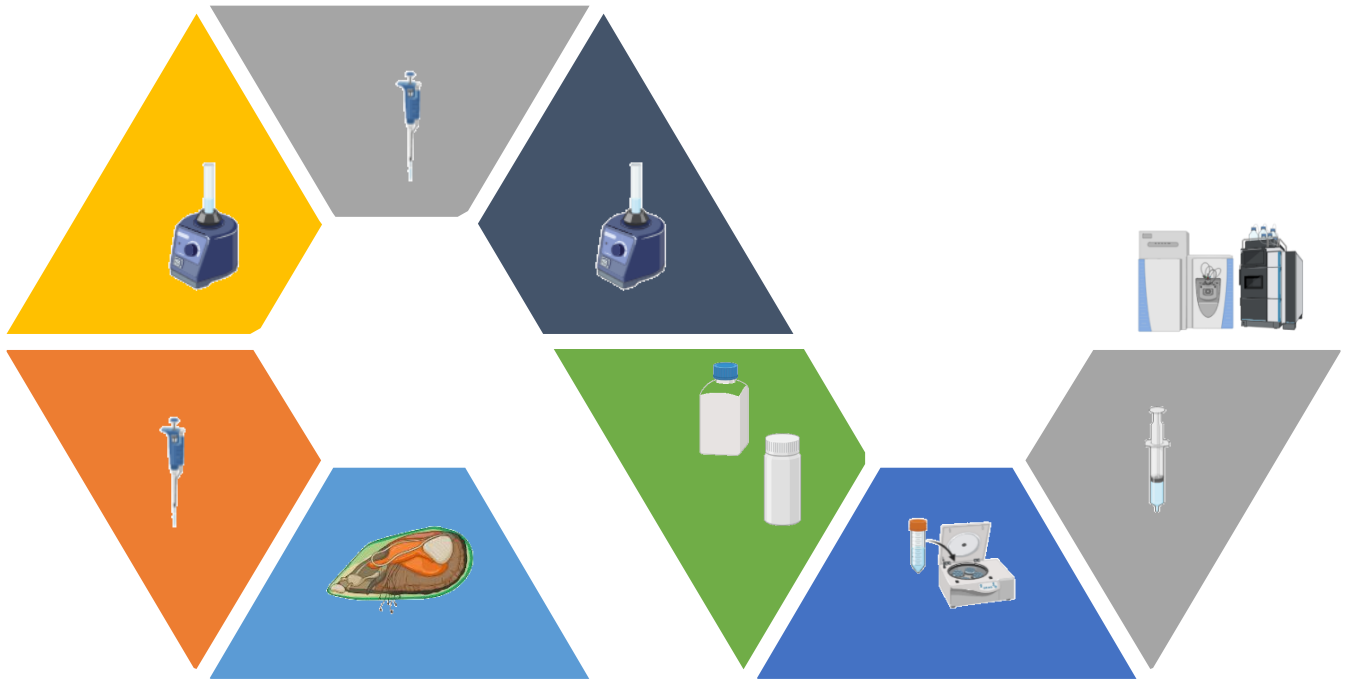


*LOD
*LOQ
*RSD_R
*RSD_r

Evaluated Protocols

04

- 18 samples



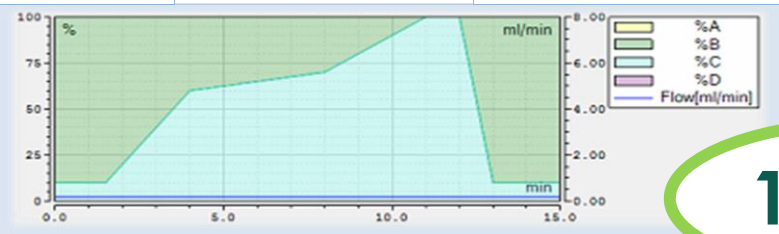
- Mussels, cockles

- October 2022, February 2023, March 2023

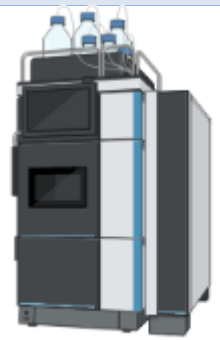
Instrumental analysis

- Thermo Scientific™ Vanquish™ Flex UHPLC
- Column Thermo Hypersil Gold aQ C18 (50 x 2.1, 1.9 µm)

Time (min)	% A (H2O+0,1% FA)	% B (MeOH+0,1% FA)
0.00	90.00	10.00
1.50	90.00	10.00
4.00	40.00	60.00
8.00	30.00	70.00
11.00	0.00	100.00
12.00	0.00	100.00
13.00	90.00	10.00
15.00	90.00	10.00



15 min



- Flow rate: 200 uL min^{-1}
- Injection volume: 5 uL

- HESI probe
- Negative ionization mode
- FS mode: 100-1000 *m/z*
- Resolution: 70.000

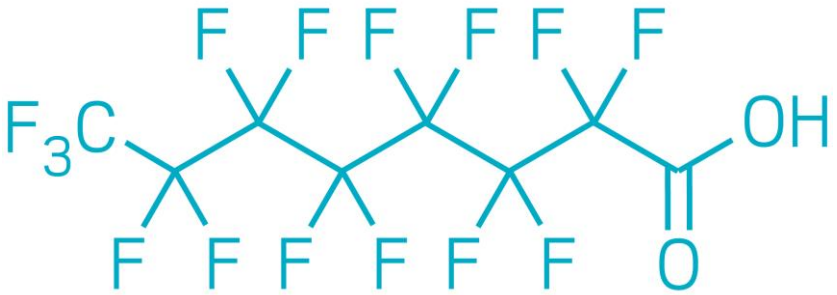
Parameters	Values
Sheath gas	45 au
Auxiliary gas	10 au
Sweep gas	2 au
Tube lens	110 V
Spray voltage	2.5 kV
Capillary Temp.	320°C
Acquisition	FS-ddMS

Target PFAS

Compound
4:2FtS
6:2FtS
8:2FtS
L-PFBS
L-PFDoS
L-PFDS
L-PFHpS
L-PFNS
L-PFPeS
L-PFTrDS
L-PFUdS
N-EtFOSAA
N-MeFOSAA
PFBA
PFDA
PFDoA
PFHpA
PFHxA
PFHxS
PFNA
PFOA
PFOS
PFOSA
PFPeA
PFTeDA
PFTrDA
PFUdA

Quantification of target compounds

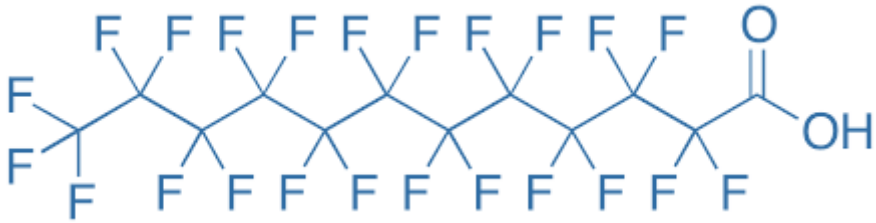
04



PFOA

10 ng/g

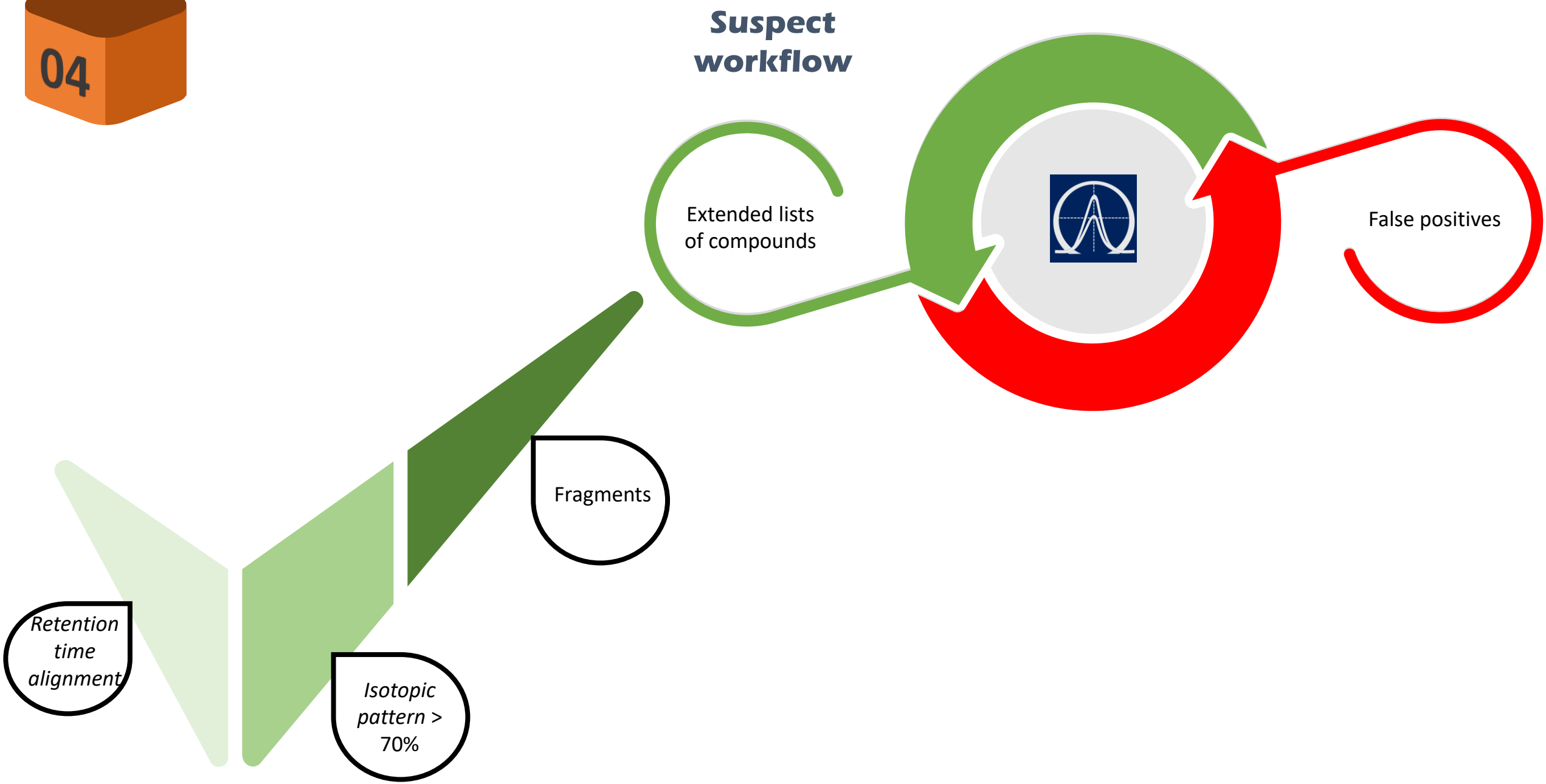
PFDoA



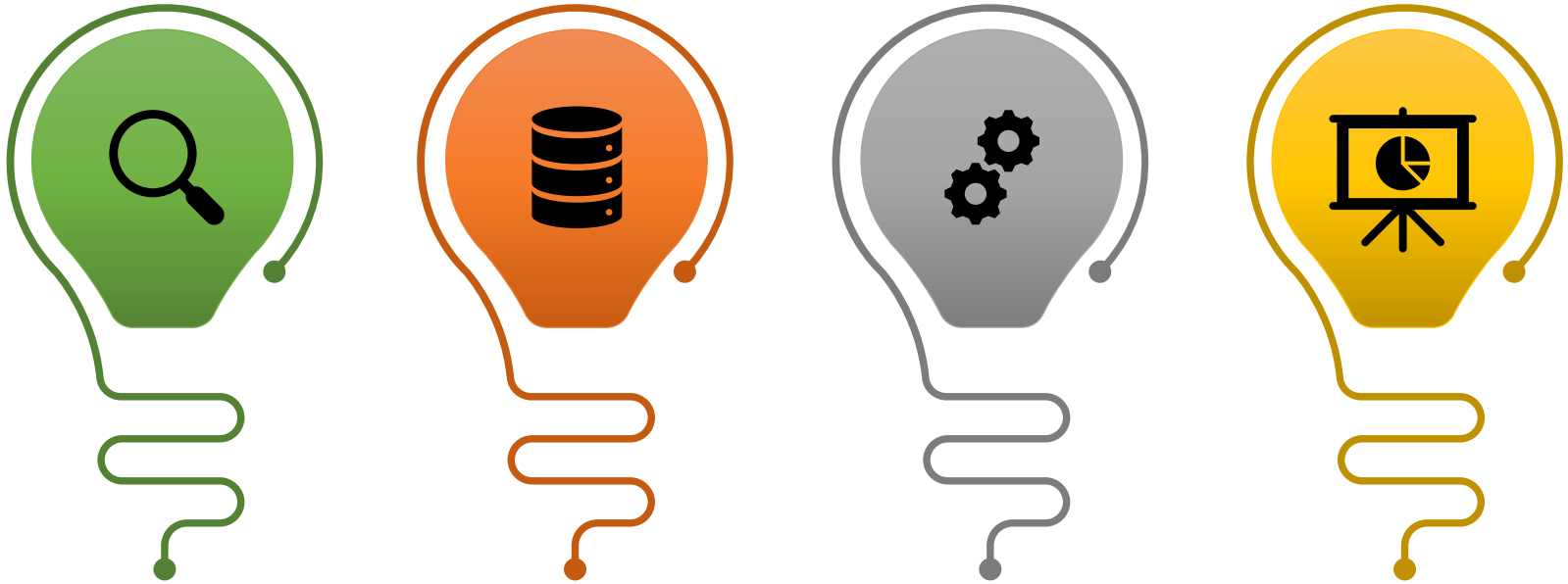
Suspect workflow

04

Suspect workflow



Suspect workflow



Combination of Norman databases

TraceFinder Database

TraceFinder method

Applied criteria

Suspect workflow

TraceFinder Compound Database Mass List Export							
Schema Version	Peak Header Line Number	Peak Last Row Line Number	Compound Header Line Number				
1	6	2669	2672				
Compound Name	**Workflow**	**Associated Target Peak**	**MS Order**	**Precursor m/z**	**Product m/z**	**m/z**	**Height Th**
compound 1	TargetPeak		ms1	0	531.0986	531.0986	5000
compound 10	TargetPeak		ms1	1	455.9581	455.9581	5000
compound 100	TargetPeak		ms1	2	557.0016	557.0016	5000
compound 1000	TargetPeak		ms1	3	608.8451	608.8451	5000
compound 1001	TargetPea		ms1	4	493.0603	493.0603	5000
compound 1002	TargetP		ms1	5	323.9264	323.9264	5000
compound 1008	Target		ms1	6	864.9697	864.9697	5000
compound 1009	Target		ns1	7	452.9529	452.9529	5000
compound 101	Target		ns1	8	454.9924	454.9924	5000
compound 1010	Target		ns1	9	475.0360	475.0360	5000
compound 1011	Target		ms1	10	503.0673	503.0673	5000
compound 1012	TargetP		ms1	11	517.0830	517.0830	5000
compound 1013	TargetPea		ms1	12	198.0159	198.0159	5000
compound 1014	TargetPeak		ms1	13	860.8431	860.8431	5000
compound 1015	TargetPeak		ms1	14	1058.1023	1058.1023	5000

>2500 compounds

Suspect workflow

Perfluorooctanoic acid
1,1,1,2,2,3,3,4,4-Nonafluoro-6-[(prop-2-en-1-yl)oxy]hexane
3-methyl-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopentane-1,1-dicarboxylic Acid
3H,3H-Perfluoroheptane-2,4-dione
2-{[4-(Heptafluoropropyl)phenyl]methyl}oxirane
4,4,5,5,6,6,7,7,7-Nonafluoroheptyl 2-methylprop-2-enoate
1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Henicosafluorooctacosane
(Perfluorohexyl)ethylene
2-(Perfluoropropoxy)-1H,1H-perfluoropropanol
Ethyl 6-(nonafluorobutyl)-4-phenyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate
Perfluorododecanoic acid
2H-Perfluoro(5,8-dimethyl-3,6,9-trioxadodecane)
Pentadecafluorooctyl chloride

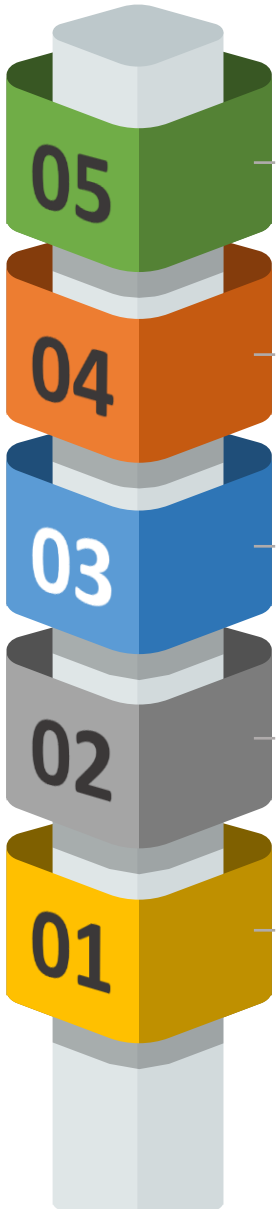
Suspect workflow

Suspect workflow

Suspect workflow

Thessaloniki
Pieria
Makrygialos
Peraia

Outline of presentation



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Take home messages…

05

4 different pretreatment protocols were evaluated in terms of recoveries

Only PFOA & PFDoA were quantified in low ng/g concentrations

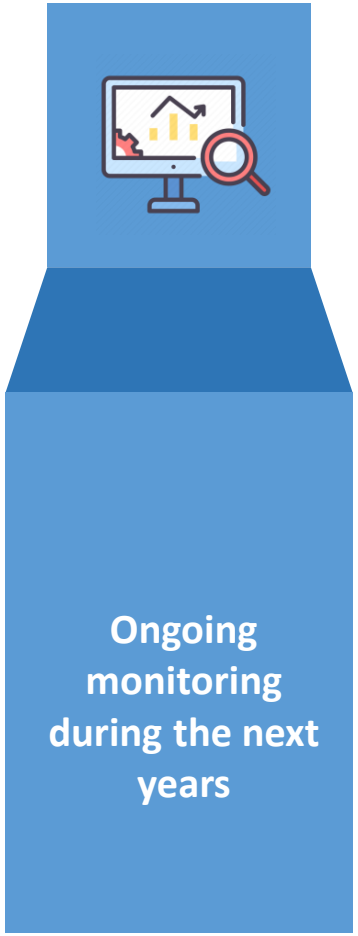
Development and implementation of a workflow for suspect PFAS

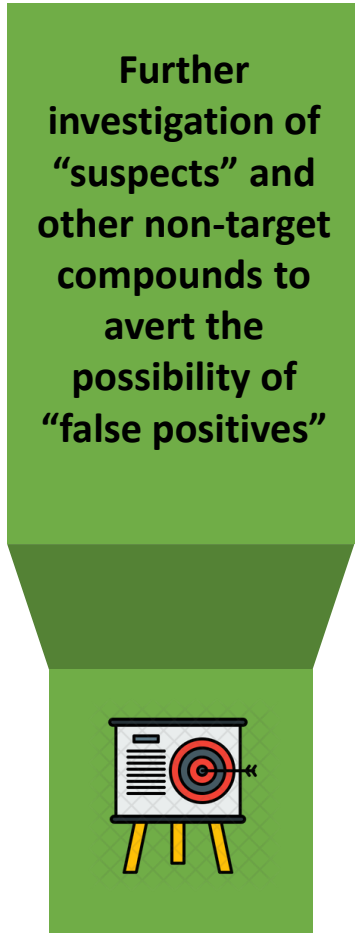
>10 short-chain PFAS were revealed

Take home messages…

05

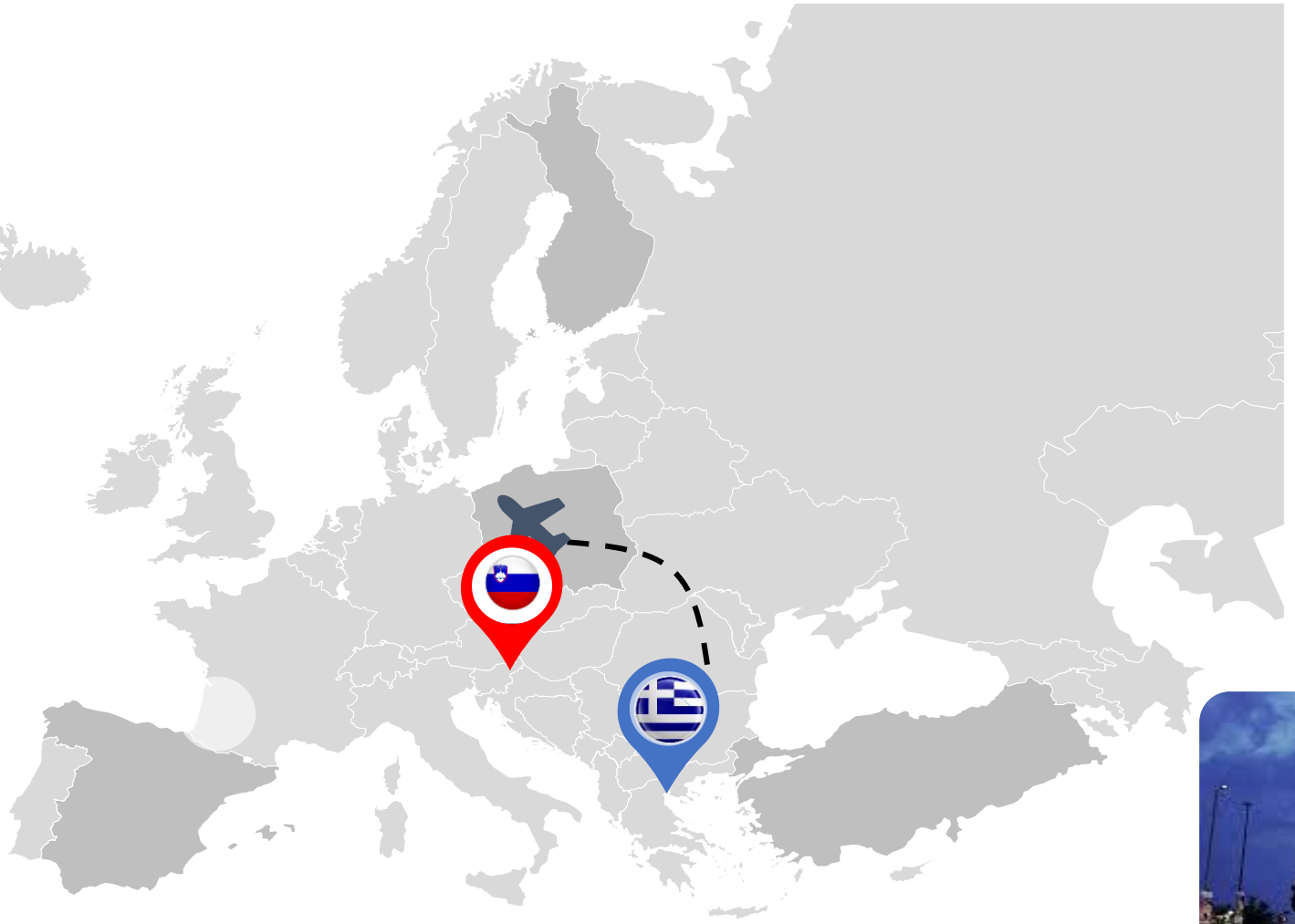
LOADING...





Portorož, Slovenia

24-26/04/2023



Thessaloniki, Greece

Safety Quality Traceability

Join our team through social media!

ENVMS Group AUTh

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https://users.auth.gr/dlambro/contact.html

dlambro@chem.auth.gr

+30 2310 99 7687

thank you

ENVMS Group

High-Resolution Mass Spec

H.F.R.I. Hellenic Foundation for Research & Innovation

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PFAS4Risks