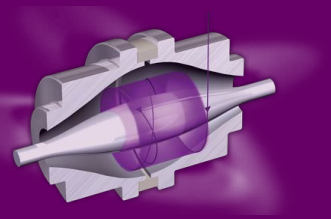
HRMS strategies for the target analysis and suspect screening of persistent and mobile substances in drinking, ground and surface water of Greece



Kyriaki Anagnostopoulou, Eleni Evgenidou, Dimitra Lambropoulou

Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, Greece

Center for Interdisciplinary Research and Innovation (CIRI-AUTH), Balkan Center, Thessaloniki, 57001, Greece

R
E
A
C
H

PM Compounds

Identifiable organic chemical >0.1%

R

E

A

C

H

PM Compounds

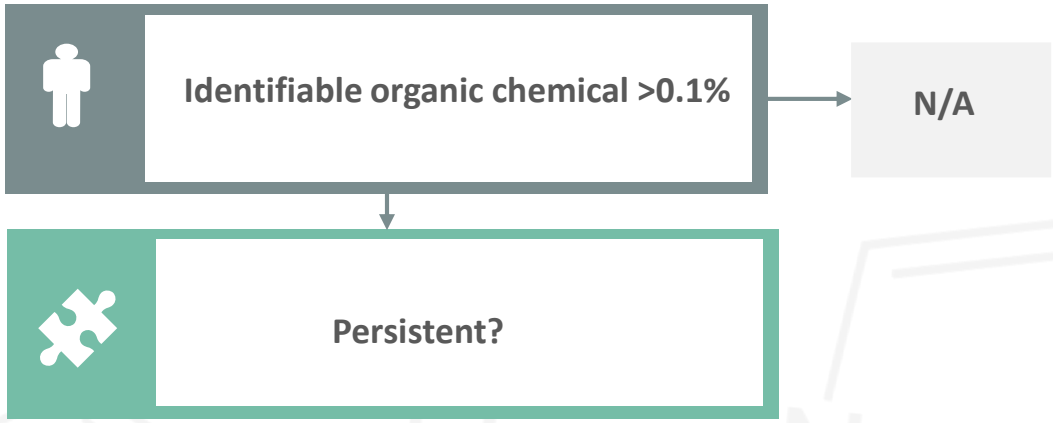
R

E

A

C

H



PM Compounds

R

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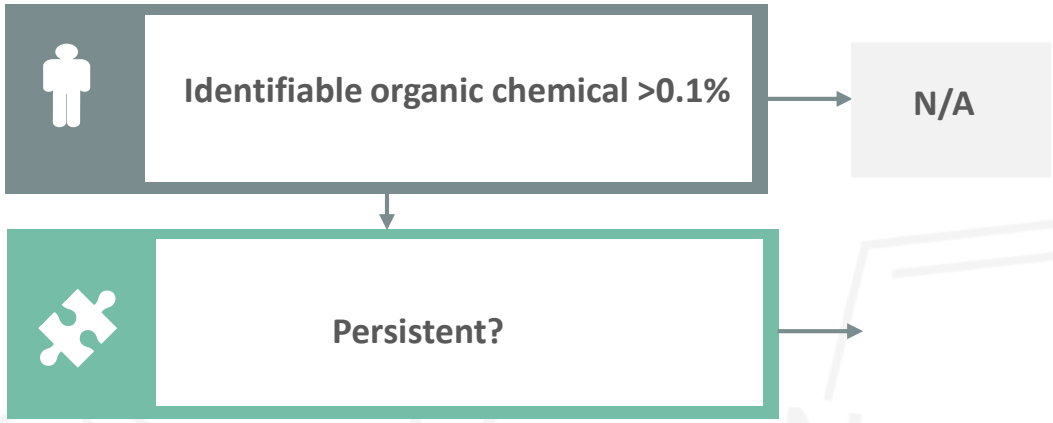

PM Compounds

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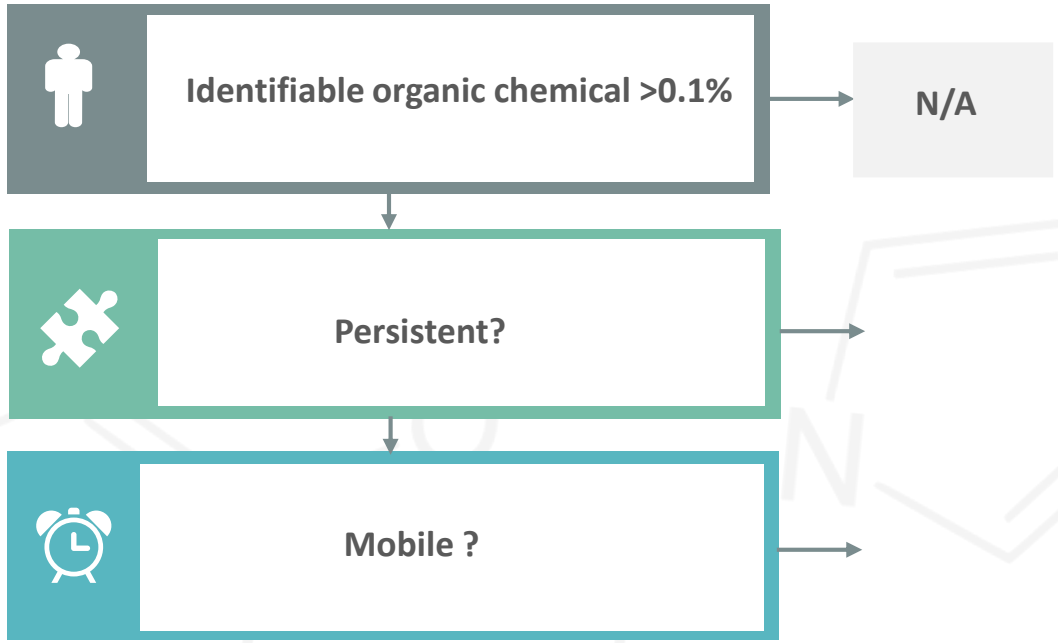
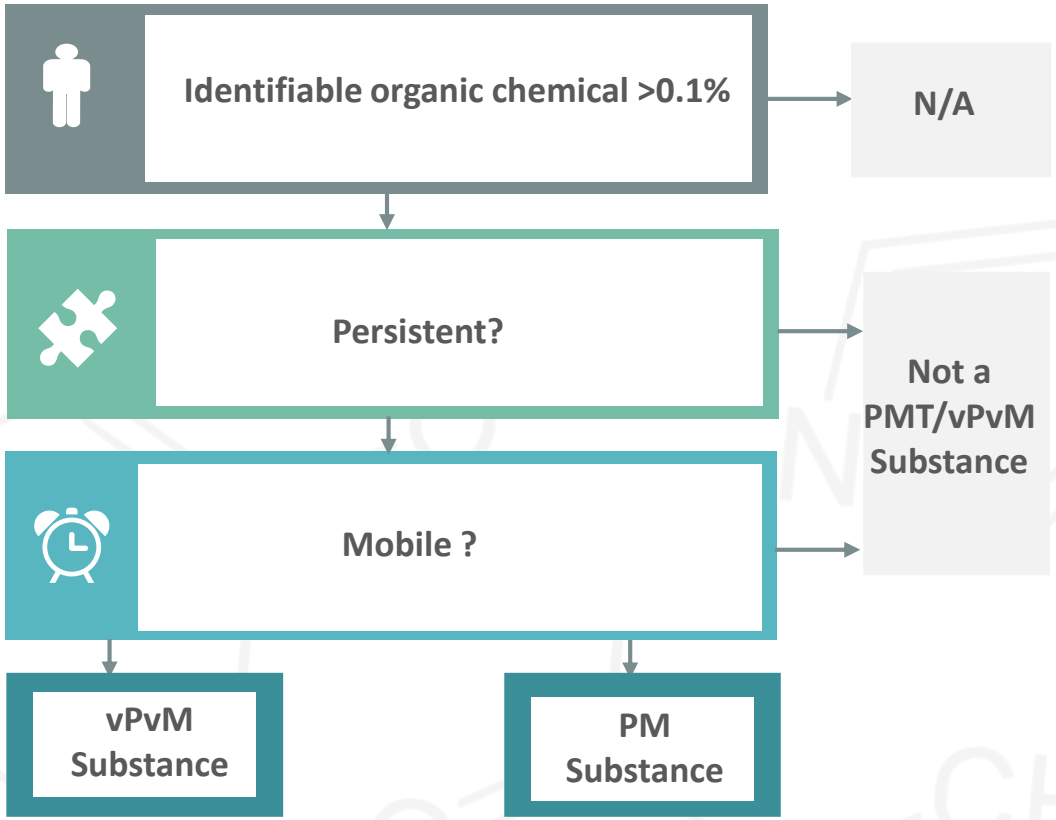


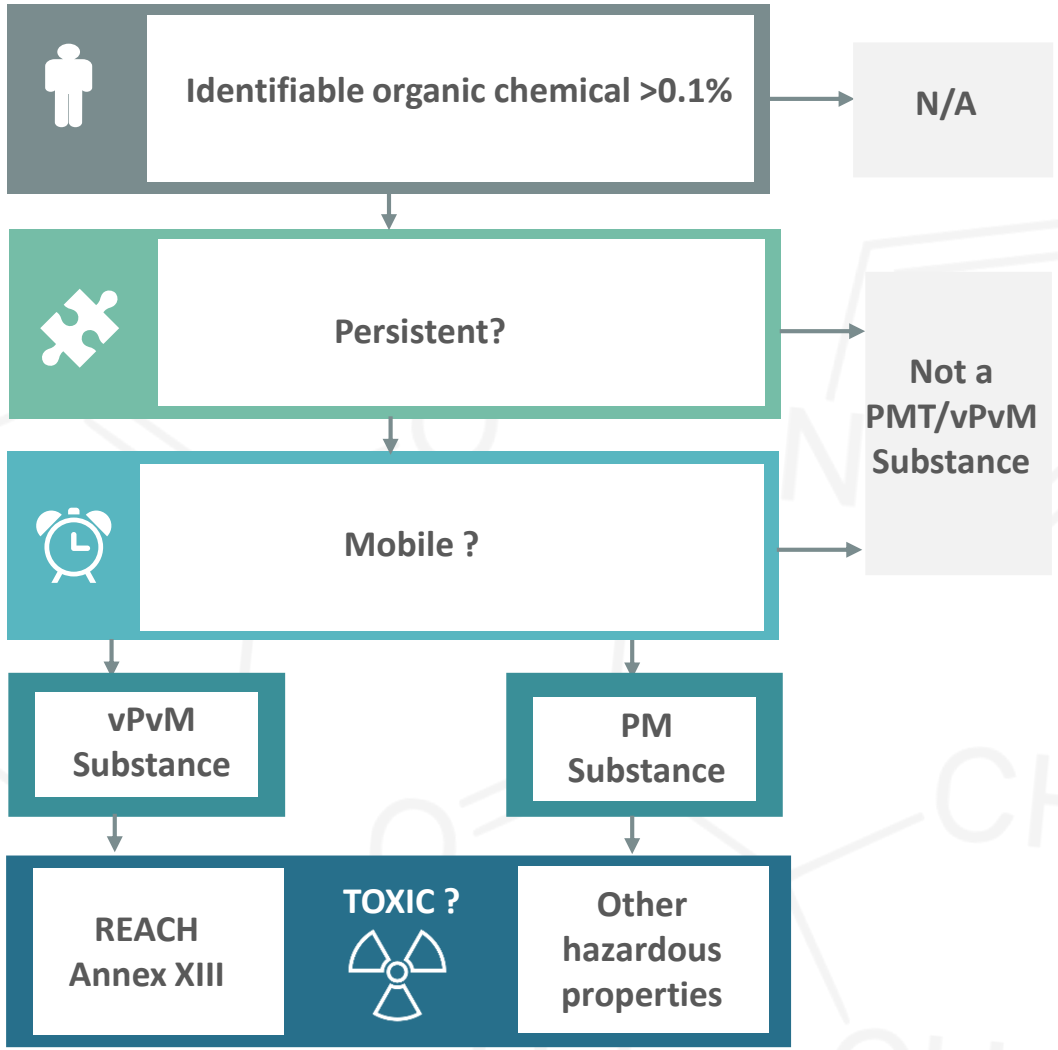
PM Compounds

R E A C H



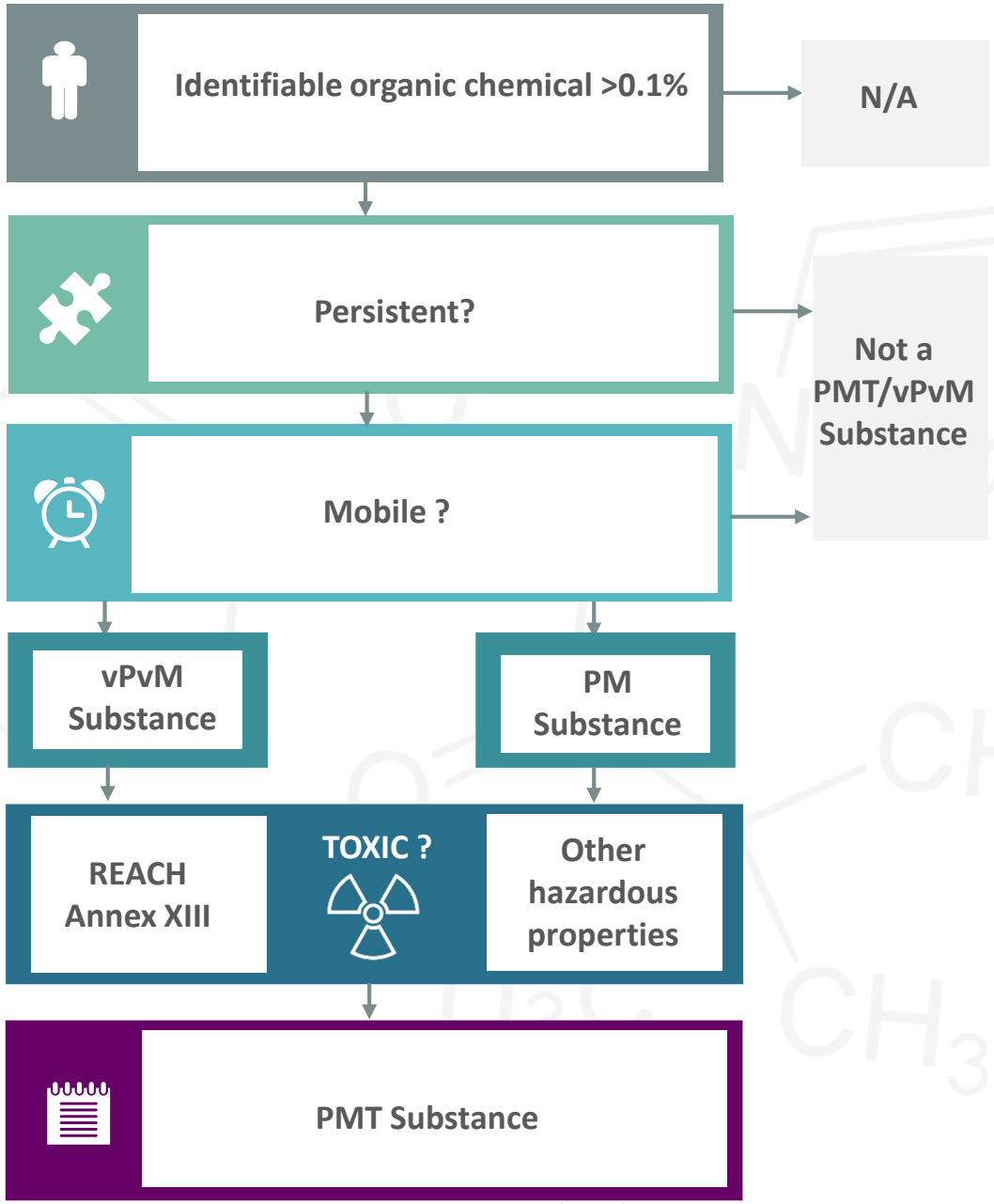
PM Compounds

R E A C H



PM Compounds

R E A C H



Neumann and Schliebner (2019)

PM Compounds

P/vP Criteria

A substance fulfils the **persistent** / **"very persistent"** criterion **(P) /(vP)**
The degradation half-life:

- in marine water at 9 °C is higher than **60 days**
- in fresh or estuarine water at 12 °C and pH 4-9 is higher than **40 days /60 days**
- in marine sediment at 9 °C is higher than **180 days**
- in fresh or estuarine water sediment at 12 °C and pH 4-9 is higher than **120 days /180 days**
- in soil at 12 °C and pH 4-9 is higher than **120 days /180 days**

M/vM Criteria

A substance fulfils the **mobile** criterion **(M):**

- The lowest organic carbon-water coefficient log K_{OC} over the pH range of 4-9 is less than **4.0**

A substance fulfils the **"very mobile"** criterion **(vM):**

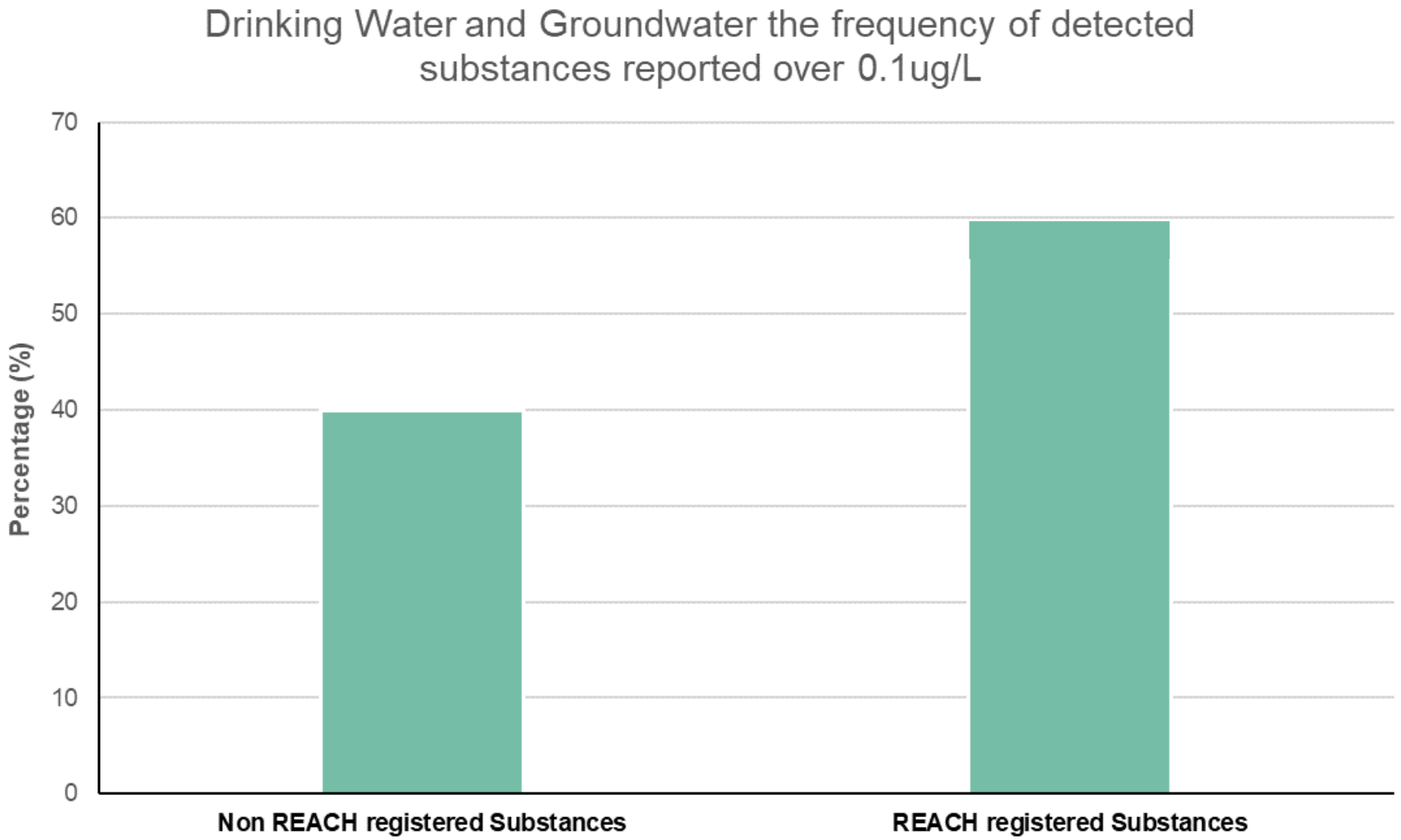
- the lowest organic carbon-water coefficient log K_{OC} over the pH range of 4-9 is less than **3.0**

If no KOC data is available

- *octanol-water partition coefficient (KOW) or*
- *pH-dependant octanol-water coefficient for ionisable substances (DOW)*

PM Compounds

P/vP Criteria



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A substa
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If no KOC c
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/180 days

M/vM Criteria

PM Compounds

Science of the Total Environment 865 (2023) 161228

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Persistence and Mobility (defined as organic-carbon partitioning) do not correlate to the detection of substances found in surface and groundwater: Criticism of the regulatory concept of Persistent and mobile substances

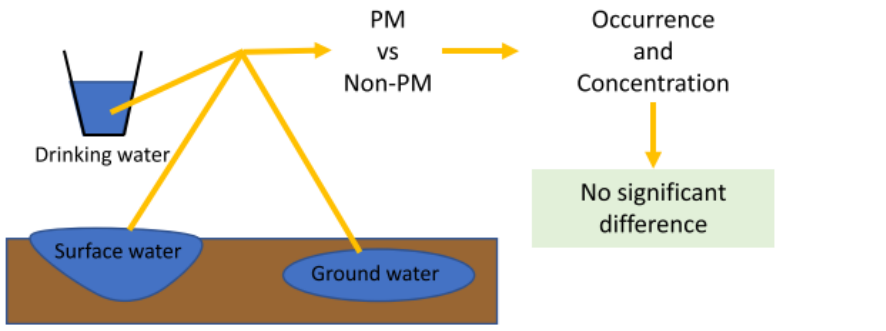
Marie Collard [a], Louise Camenzuli [b], Delina Lyon [c,*], David Saunders [d], Nathalie Vallotton [e], Pippa Curtis-Jackson [f]

[a] Firmenich SA, Louvain-la-neuve, Belgium
[b] ExxonMobil Petroleum and Chemical BV, Machelen, Belgium
[c] Concawe, Boulevard du Souverain 165, B-1160 Brussels, Belgium
[d] Shell International, The Hague, Netherlands
[e] Dow Europe GmbH, Horgen, Switzerland
[f] Environment Agency, Bristol, United Kingdom

HIGHLIGHTS

- PM substances do not have a higher likelihood of detection than non-PM substances.
- Likelihood of detecting a P substance in water is independent of the M criterion.
- There is no indication that PM substance accumulate in water bodies.
- No evidence of log Dow or log Koc as driver of contamination of water.

GRAPHICAL ABSTRACT



PM Compounds

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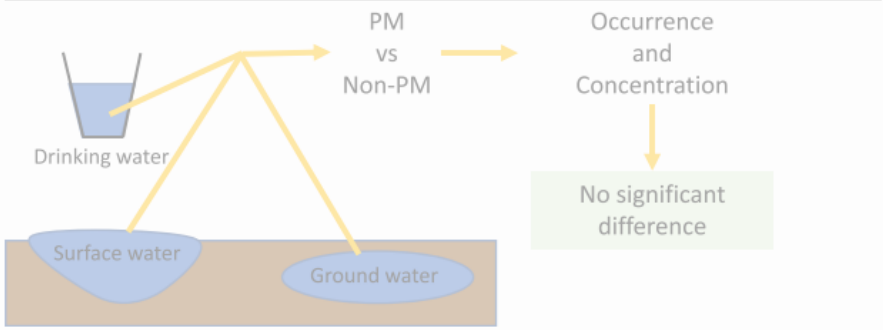

PM Compounds

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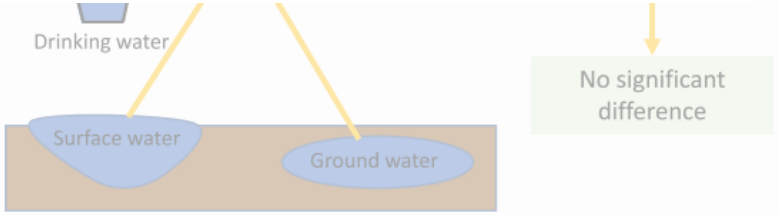

PM Compounds

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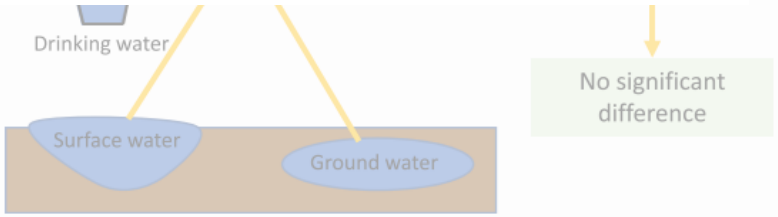

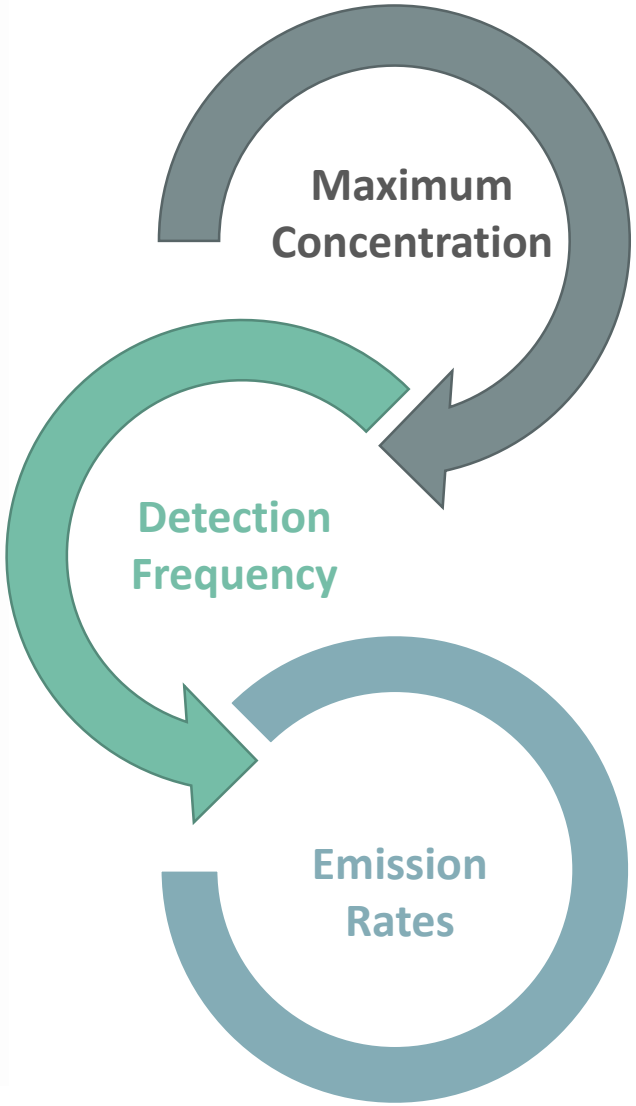

PM Compounds

Water Research 204 (2021) 117645

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Filling the knowledge gap: A suspect screening study for 1310 potentially persistent and mob river systems

Isabelle Neuwald [a,1], Ma
Till Meier [b], Jochen Kuc
Thorsten Reemtsma [b,d,*]

[a] Hochschule Fresenius gem. GmbH, Limb
[b] Department of Analytical Chemistry, He
[c] Umweltbundesamt, Section Toxicology o
[d] University of Leipzig, Institute for Analyt

ARTICLE INFO

Keywords:
PMT-substances
Wastewater
Groundwater
Drinking water
Water cycle
LC-MS

Water Research 153 (2019) 80–90

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate

Occurrence of emerging persistent and mobile organic in European water samples

Stefanie Schulze [a], Daniel Zahn [b], Rosa Montes [c], Rosario Rodil [c], José
Thomas P. Knepper [b], Thorsten Reemtsma [a,d], Urs Berger [a,*]

[a] Helmholtz Centre for Environmental Research – UFZ, Department of Analytical Chemistry, Permoserstrasse 15, 04318,
[b] Hochschule Fresenius University of Applied Sciences, Institute for Analytical Research, Limburger Strasse 2, 65510, Idst
[c] Universidade de Santiago de Compostela, Department of Analytical Chemistry, Nutrition and Food Sciences, IIAA - Institu
Constantino Candeira S/N, 15782, Santiago de Compostela, Spain
[d] University of Leipzig, Institute of Analytical Chemistry, Linnéstrasse 3, 04103 Leipzig, Germany

ARTICLE INFO

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Keywords:
Persistent and mobile organic chemicals
PMOC
Water
Occurrence
Chromatography

ABSTRACT

The release of persistent and mobile organic chemical
quality of water resources at risk. PMOCs are challeng
polarity. The aim of this study was to develop novel
their occurrence in surface and groundwater samp
prioritized list of industrial chemicals that were mode
environment. Analytical screening methods based on
philic interaction LC, reversed phase LC, or supercritica
spectrometric detection were successfully developed
samples from three European countries. A total of 43 P
them 23 PMOCs that have not been reported before t
alent of these novel PMOCs were methyl sulfate, 2
trimethylammonium, benzyldimethylamine, trifluor
diamine, and 1,3-di-o-tolylguanidine occurring in ≥5
the low ng L^{-1} up to µg L^{-1} range. The approach of focused prioritization combined with sensitive target
chemical analysis proved to be highly efficient in revealing a large suite of novel as well as scarcely
investigated PMOCs in surface and groundwater.

Water Research 150 (2019) 86–96

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Identification of potentially mobile and persistent transformation products of REACH-registered chemicals and their occurrence in rs

Journal of Hazardous Materials Letters 2 (2021) 100026

Contents lists available at ScienceDirect

Journal of Hazardous Materials Letters

journal homepage: www.elsevier.com/locate/hazl

The distribution of persistent, mobile and toxic (PMT) pharmaceuticals and personal care products monitored across Chinese water resources

Chen Huang [a,b,c], Biao Jin [a,b,c,*], Min Han [a,b,c], Yang Yu [d], Gan Zhang [a,b], Hans Peter H. Arp [e,f]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[b] CAS Center for Excellence in Deep Earth Science, Guangzhou, 510640, China
[c] University of Chinese Academy of Sciences, Beijing, 10069, China
[d] Solid Waste and Chemicals Management Center, Ministry of Ecology and Environment (MEE), Beijing, 100029, China
[e] Norwegian Geotechnical Institute (NGI), P.O. Box 3930, Ullevaal Stadion, N-0806, Oslo, Norway
[f] Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway

ARTICLE INFO

Keywords:
Drinking water
Groundwater
Surface water
vPvM
PPCP

ABSTRACT

Hazard classifications have recently been introduced for persistent, mobile and toxic (PMT) and very persistent and very mobile (vPvM) substances, which are those that negatively impact water resources if substantially emitted into the environment. Many pharmaceuticals and personal care products (PPCPs) may meet this classification. Our study focused on 169 detected PPCPs in surface water, groundwater and drinking water in China among a total of 432 PPCPs that were monitored for across 75 studies. We assessed if these could be classified as PMT/vPvM substances based on the recent European criteria for industrial substances. For most PPCPs, persistency half-life data were lacking; therefore, definitive classifications could not be made. In surface water, 52 (37.7 %) of the detected PPCPs met, or were strongly suspected to meet, the PMT/vPvM criteria. Over half of these were antibiotic compounds. The industrialized Yangtze, Haihe and Pearl river basins were the most impacted. We hypothesized the proportion of PPCPs monitored meeting the PMT/vPvM criteria in drinking water and groundwater would be larger than surface water. This was supported as 44.3 % of PPCPs in these media met, or based on weight-of-evidence likely meet, the PMT/vPvM criteria; though, a definitive comparison was hindered by a lack of persistence data.

nown persistent and
ronment. Herein we
C precursors among
is, photolysis, MnO_2
rived transformation
posed procedure was
on was observed. For
ntified and partially
ssessment of high-
as well as a target
emicals revealed the
e (hydrolysis product
d, biotransformation
uanidine (prioritized
as detected in 23/25
TP 216 was detected
tment plant and the
plants. The vulcani-
ing experiment with
3-diphenylguanidine.
e unknowns like TP
dicted TPs to identify

PM Compounds

Target List

120 Compounds

Suspect List

2500 Compounds

Analytical Methods

Working Plan

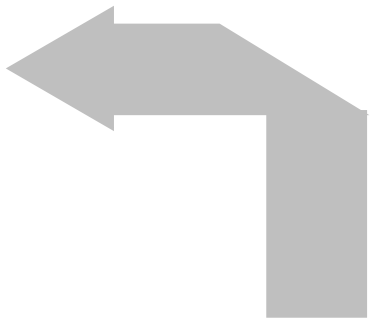
Working Plan

Literature – Inclusion List

Working Plan

Literature – Inclusion List

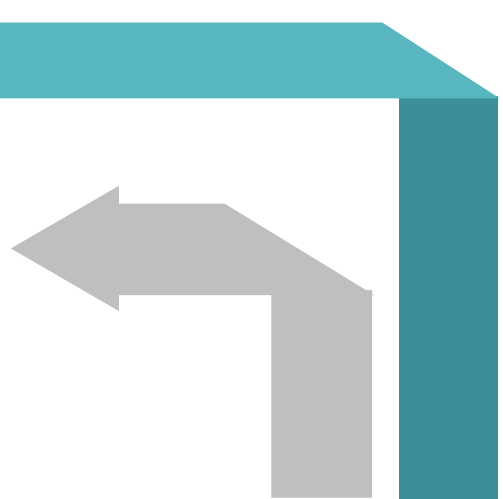
Target, Suspect Lists (potential) PM substances



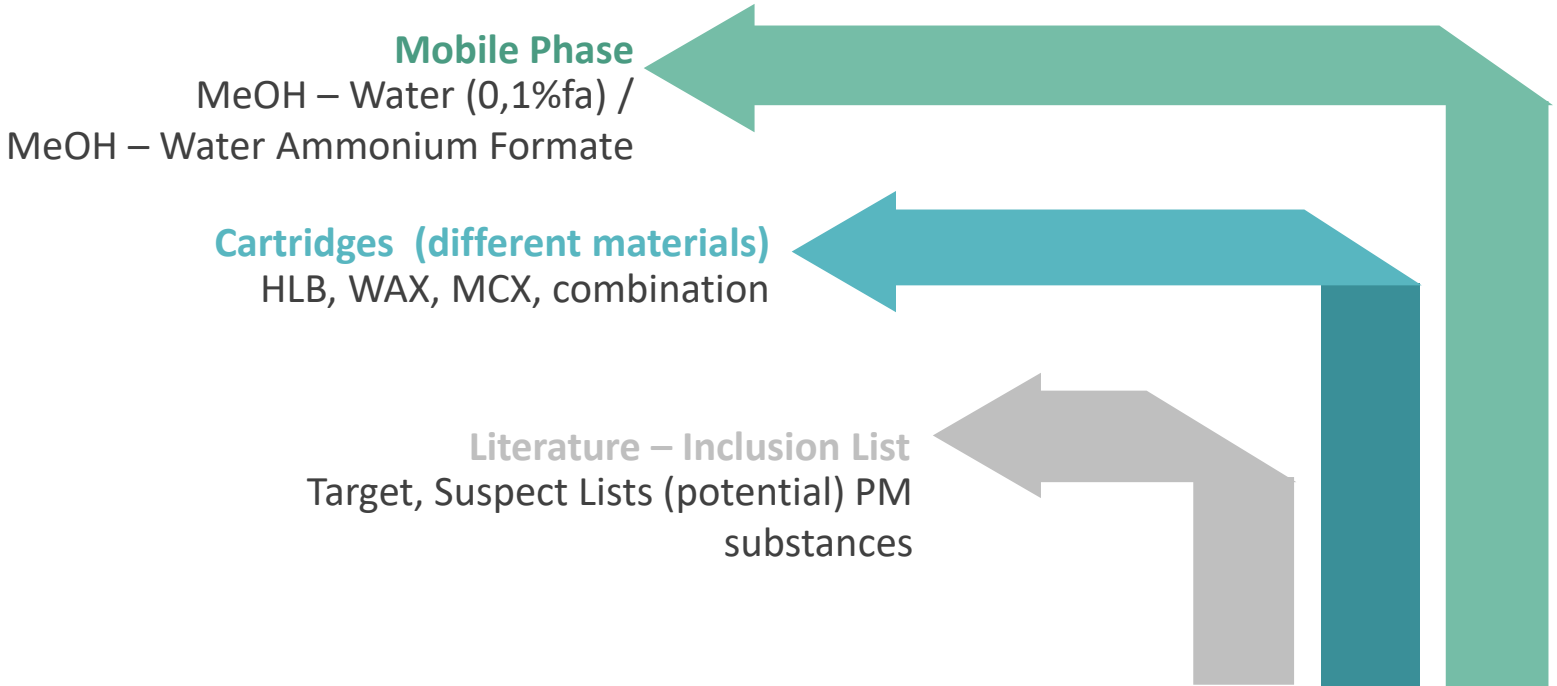
Working Plan

Cartridges (different materials)
HLB, WAX, MCX, combination

Literature – Inclusion List
Target, Suspect Lists (potential) PM substances



Working Plan



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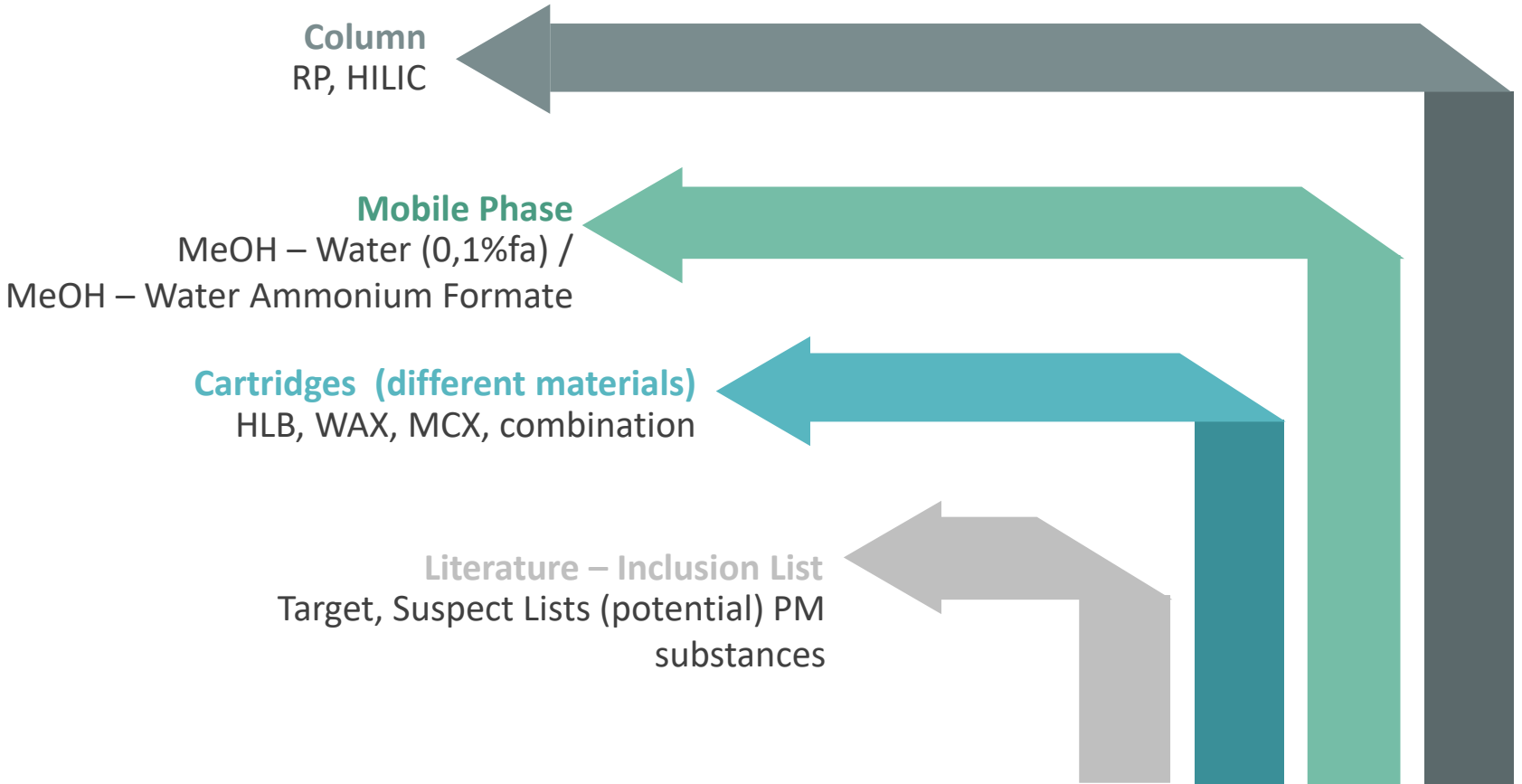

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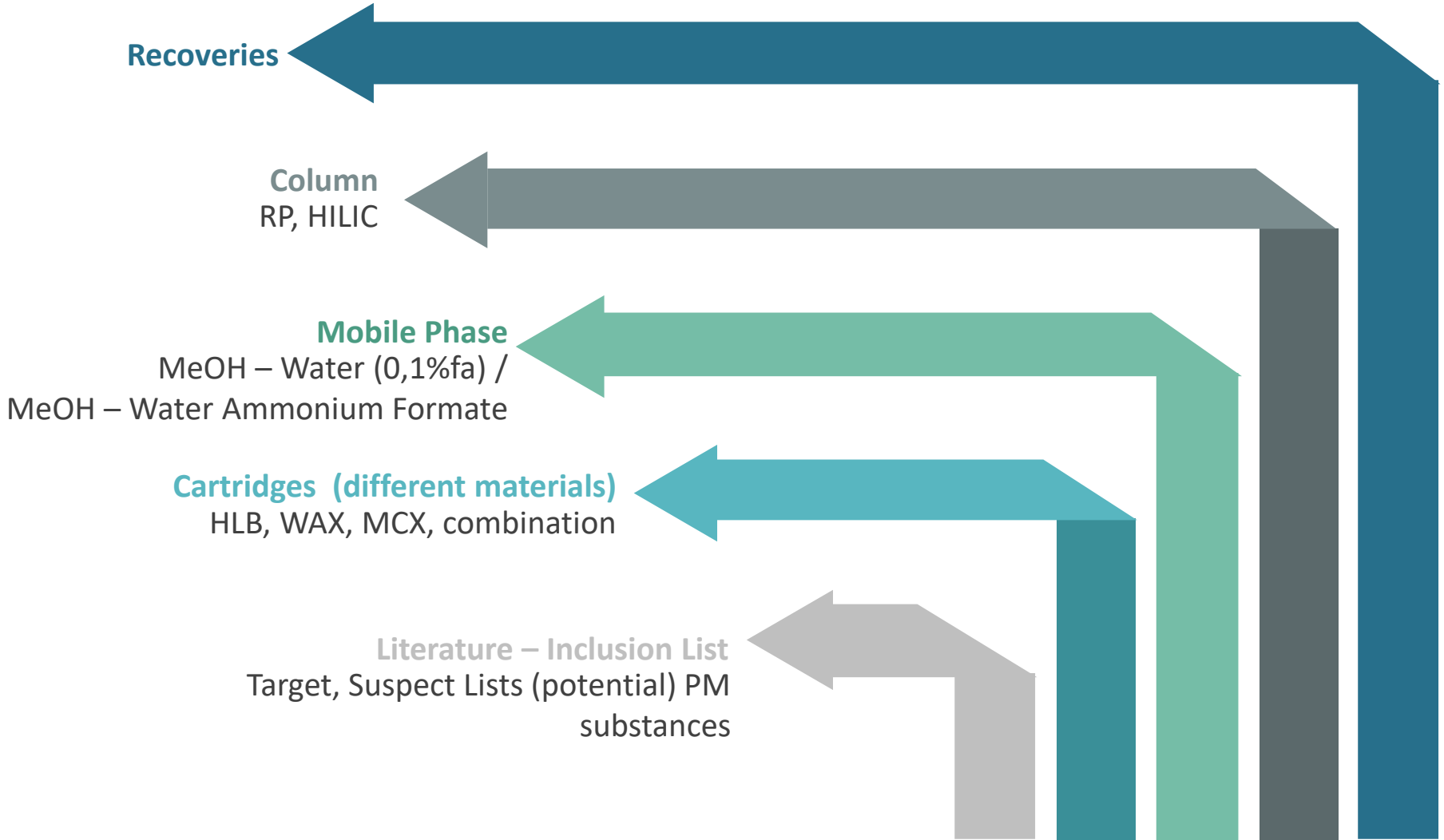

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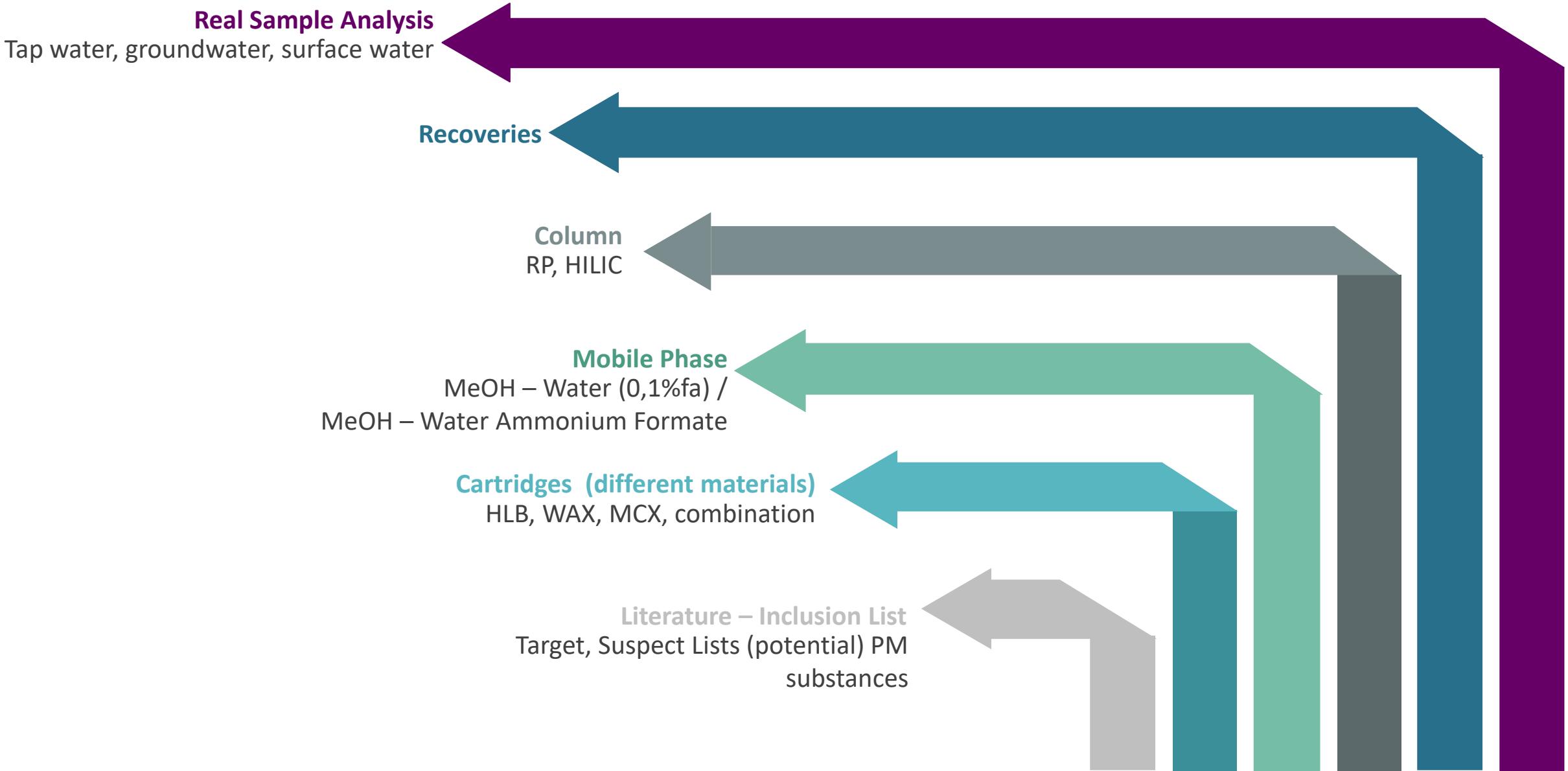
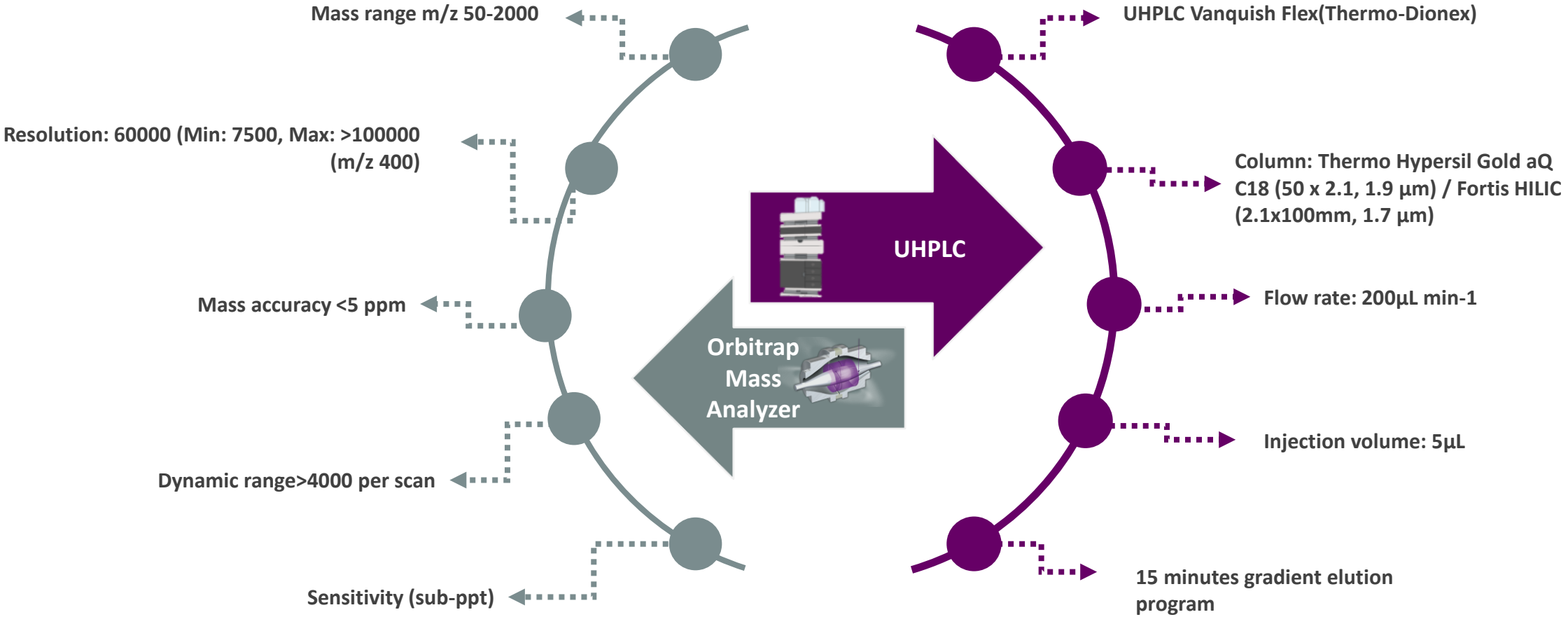
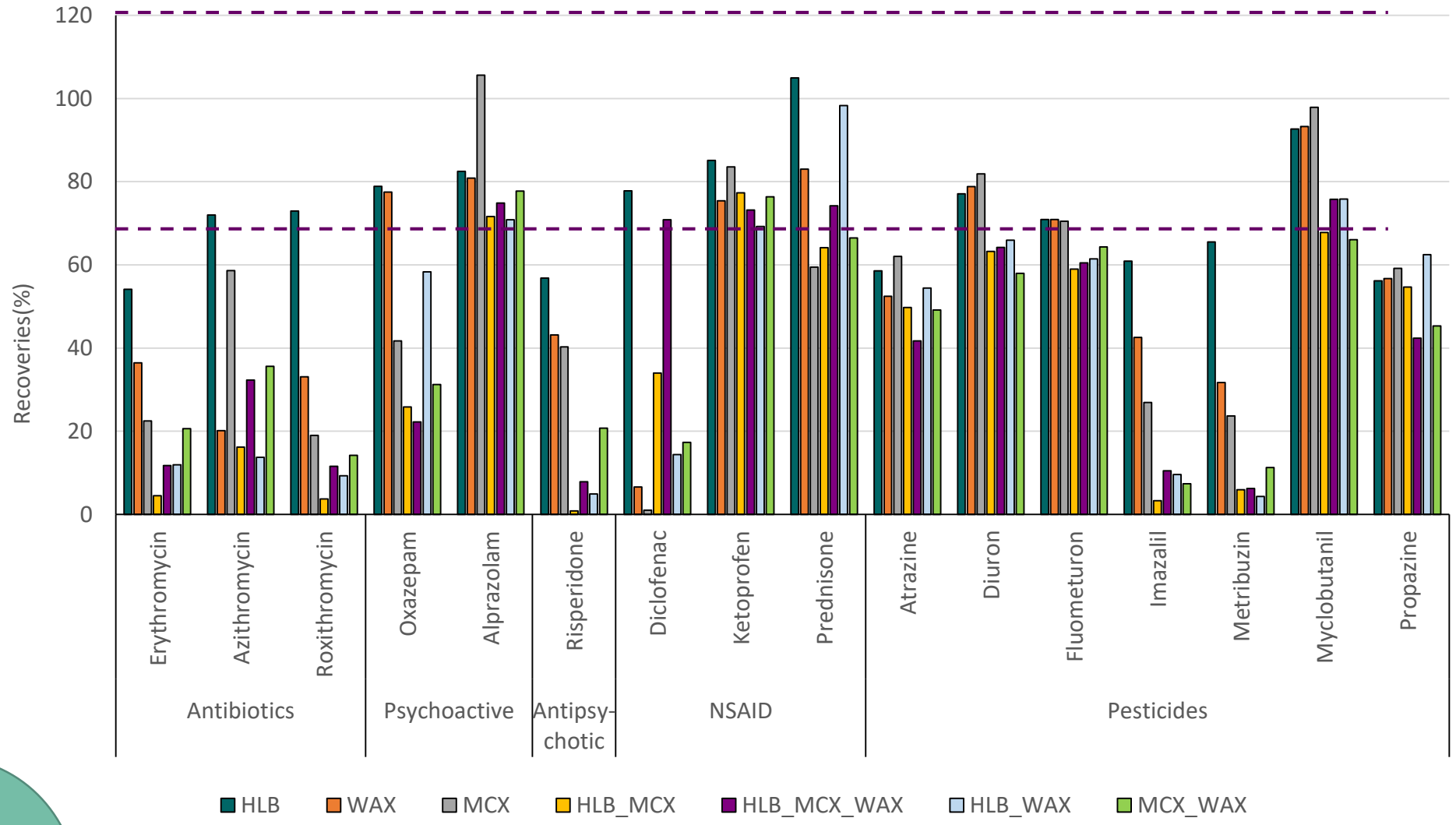


Analysis


Mass range m/z 50-2000
Resolution: 60000 (Min: 7500, Max: >100000 (m/z 400)
Mass accuracy <5 ppm
Dynamic range>4000 per scan
Sensitivity (sub-ppt)
UHPLC
Orbitrap Mass Analyzer
UHPLC Vanquish Flex(Thermo-Dionex)
Column: Thermo Hypersil Gold aQ C18 (50 x 2.1, 1.9 µm) / Fortis HILIC (2.1x100mm, 1.7 µm)
Flow rate: 200µL min-1
Injection volume: 5µL
15 minutes gradient elution program

RESULTS

Recoveries



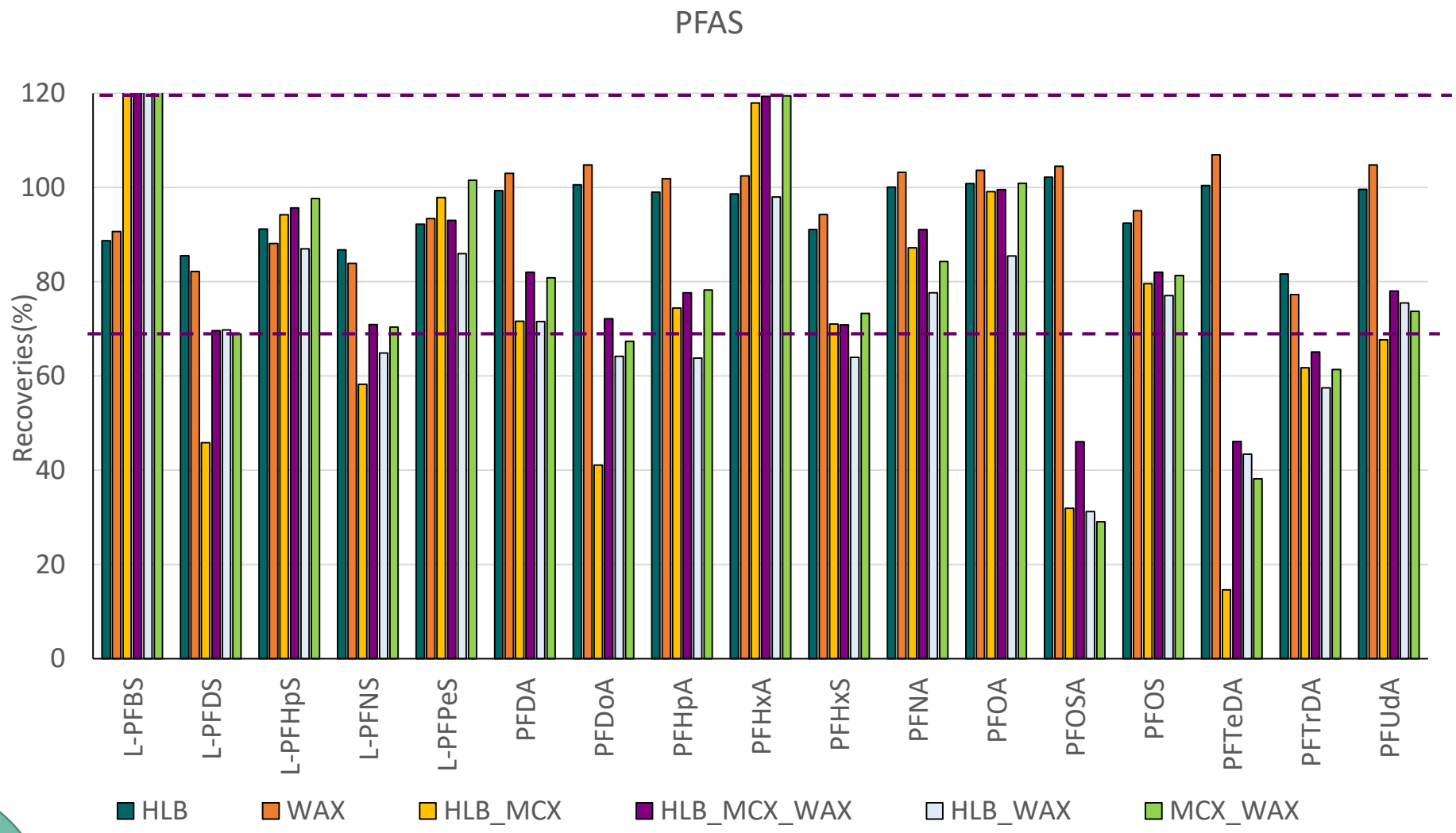
Recoveries 50-120%

↓

HLB

Cartridges

Recoveries



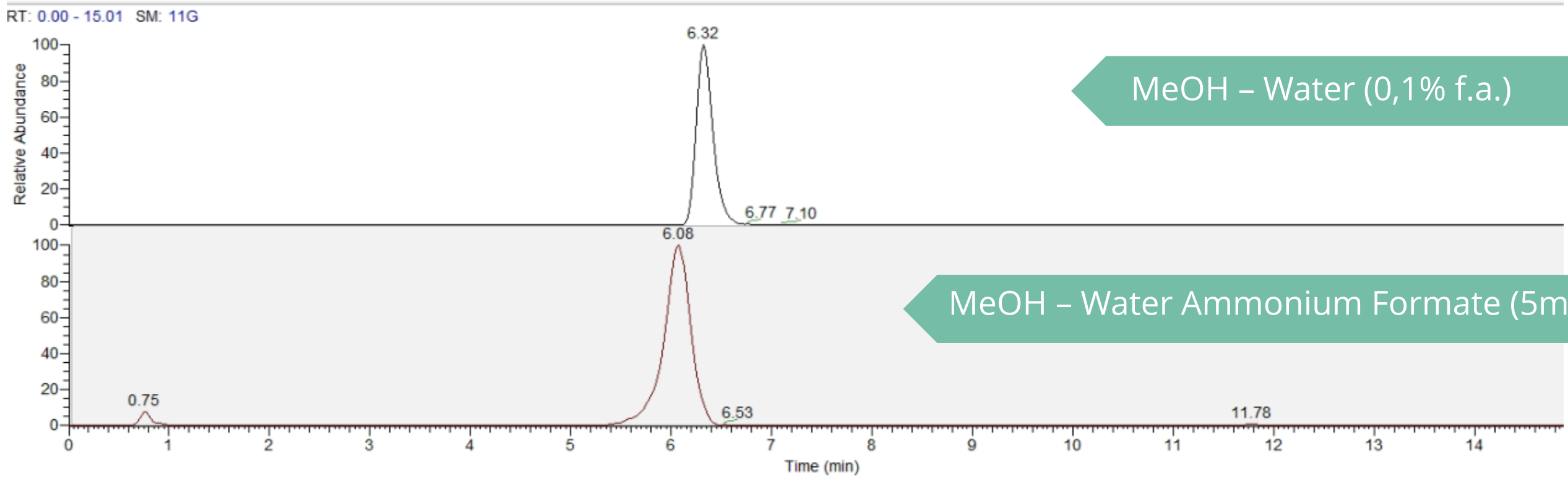
Recoveries 80-120%

↓

WAX

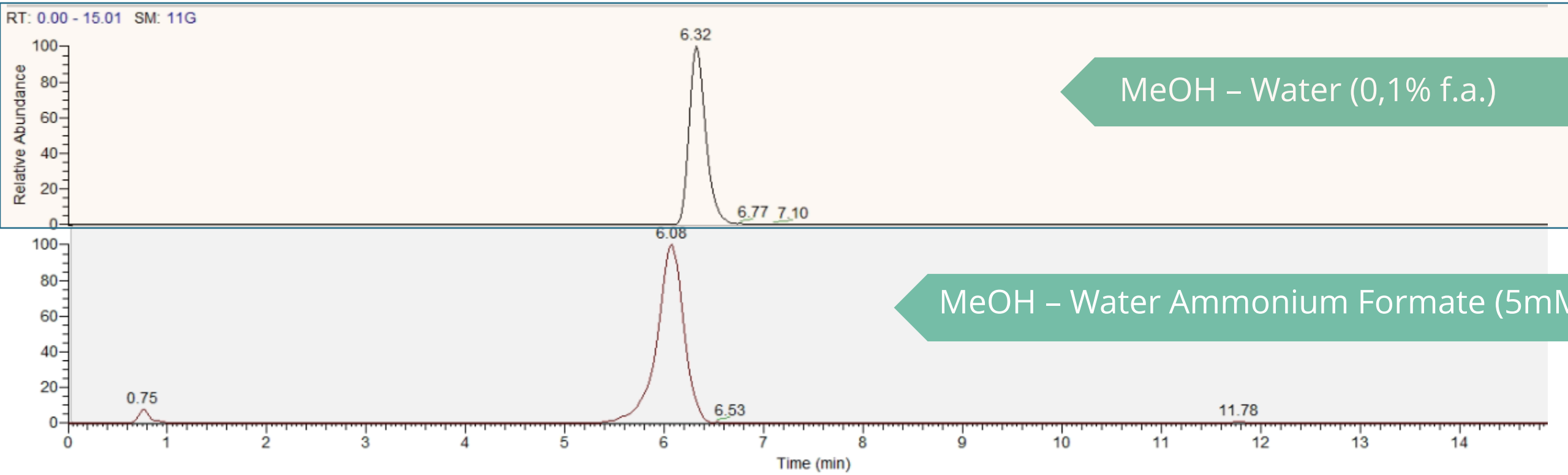
Cartridges

Peak Shape



Mobile Phase

Peak Shape

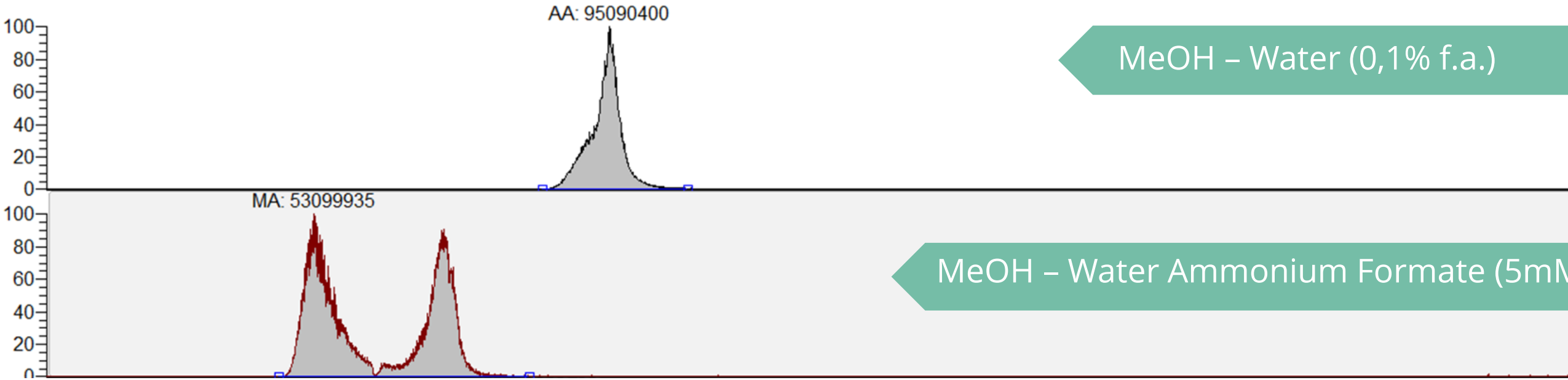


MeOH – Water (0,1% f.a.)

MeOH – Water Ammonium Formate (5mM

Mobile Phase

Peak Shape



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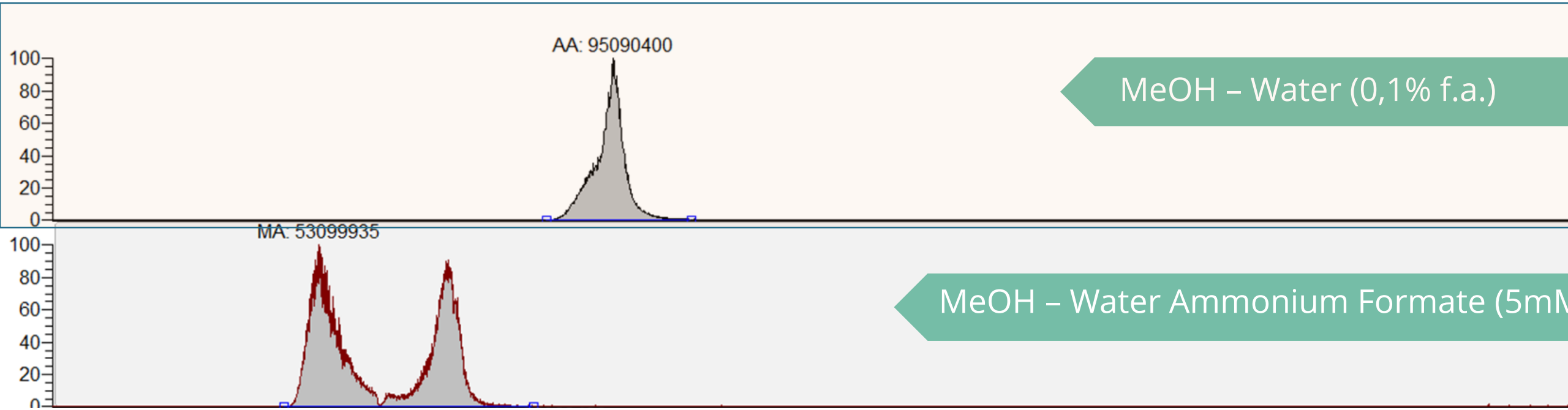
MeOH – Water Ammonium Formate (5mM

Mobile Phase

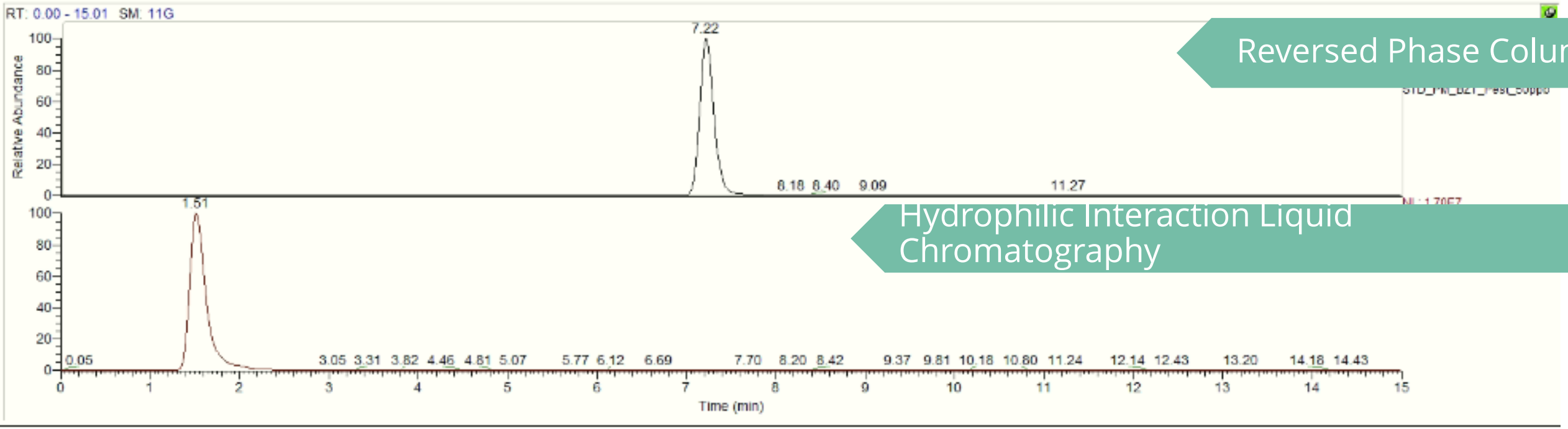
Peak Shape



Mobile Phase

Peak Shape

Column

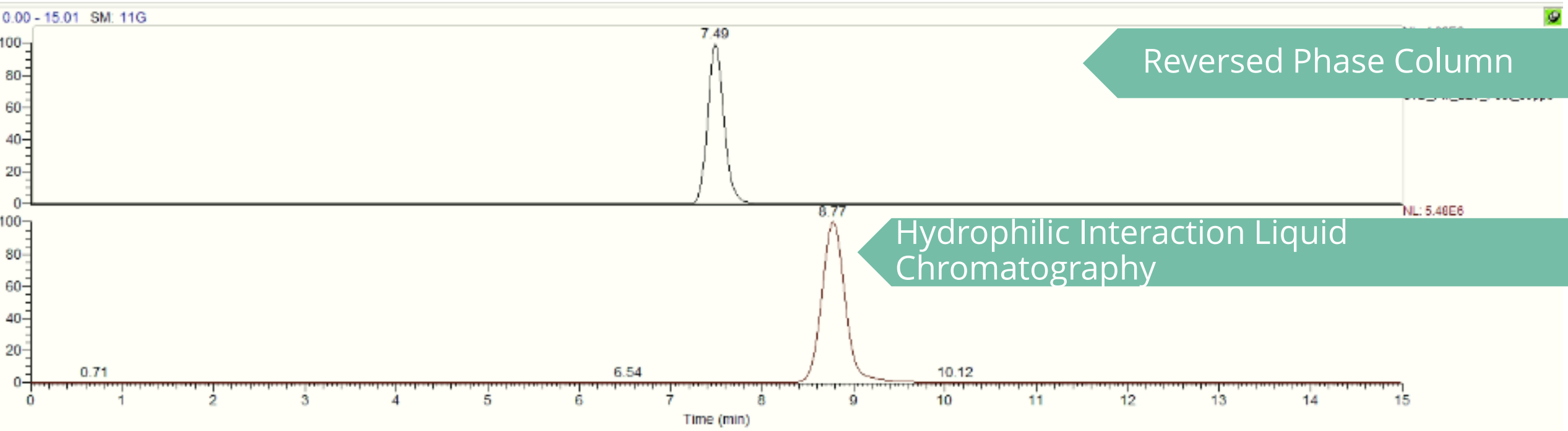


Reversed Phase Colum

Hydrophilic Interaction Liquid Chromatography

Peak Shape

Column

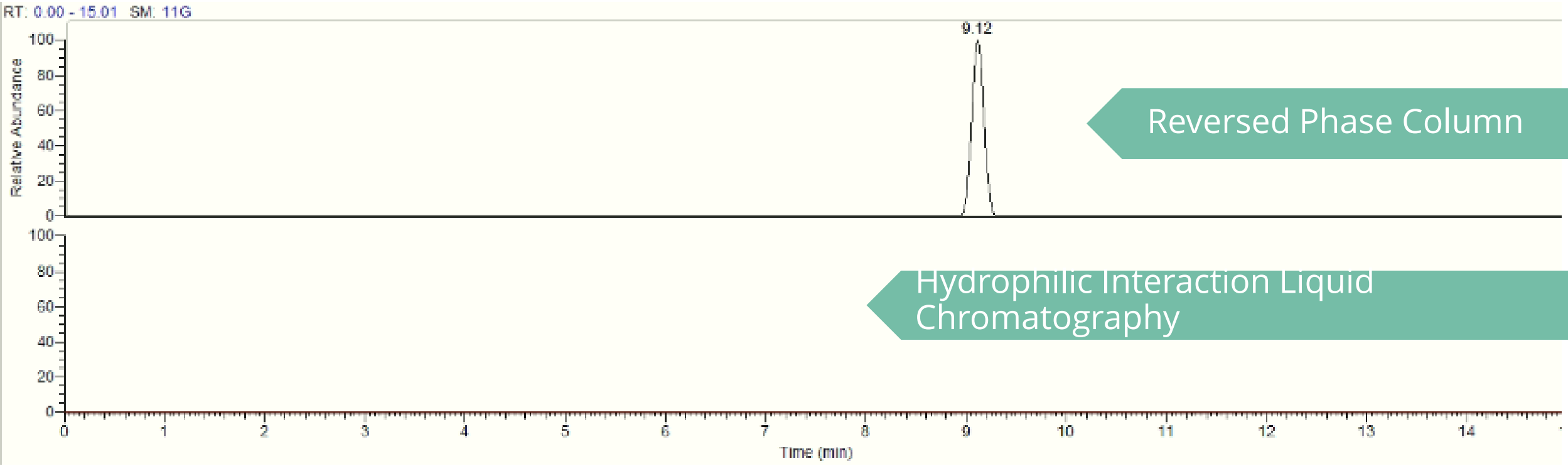


Reversed Phase Column

Hydrophilic Interaction Liquid Chromatography

Peak Shape

Column

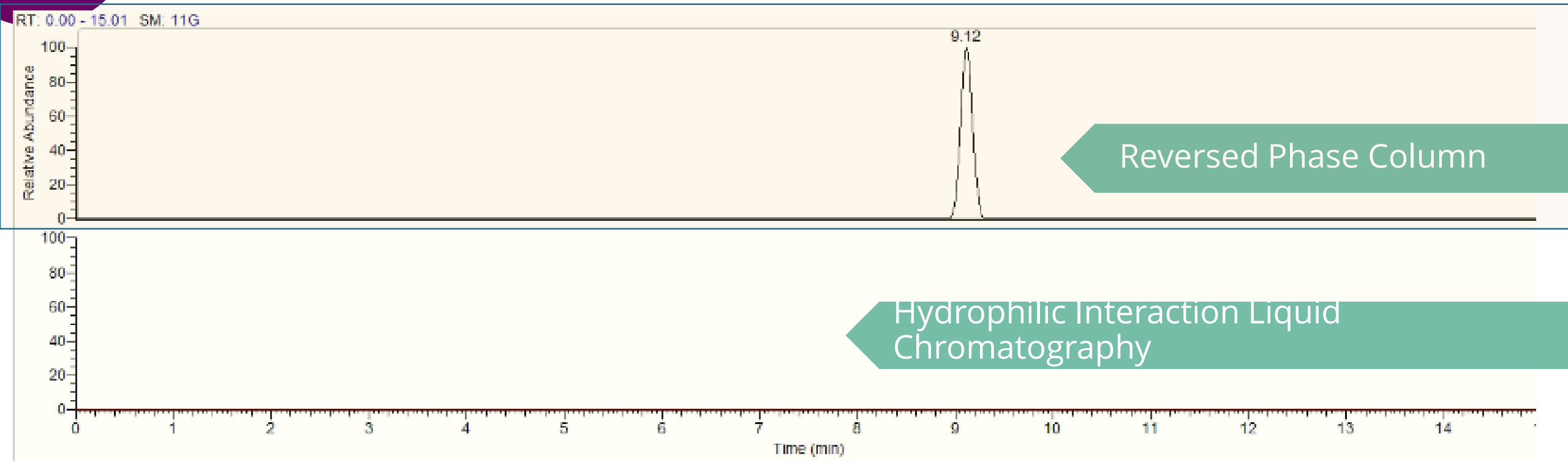


Reversed Phase Column

Hydrophilic Interaction Liquid Chromatography

Peak Shape

Column

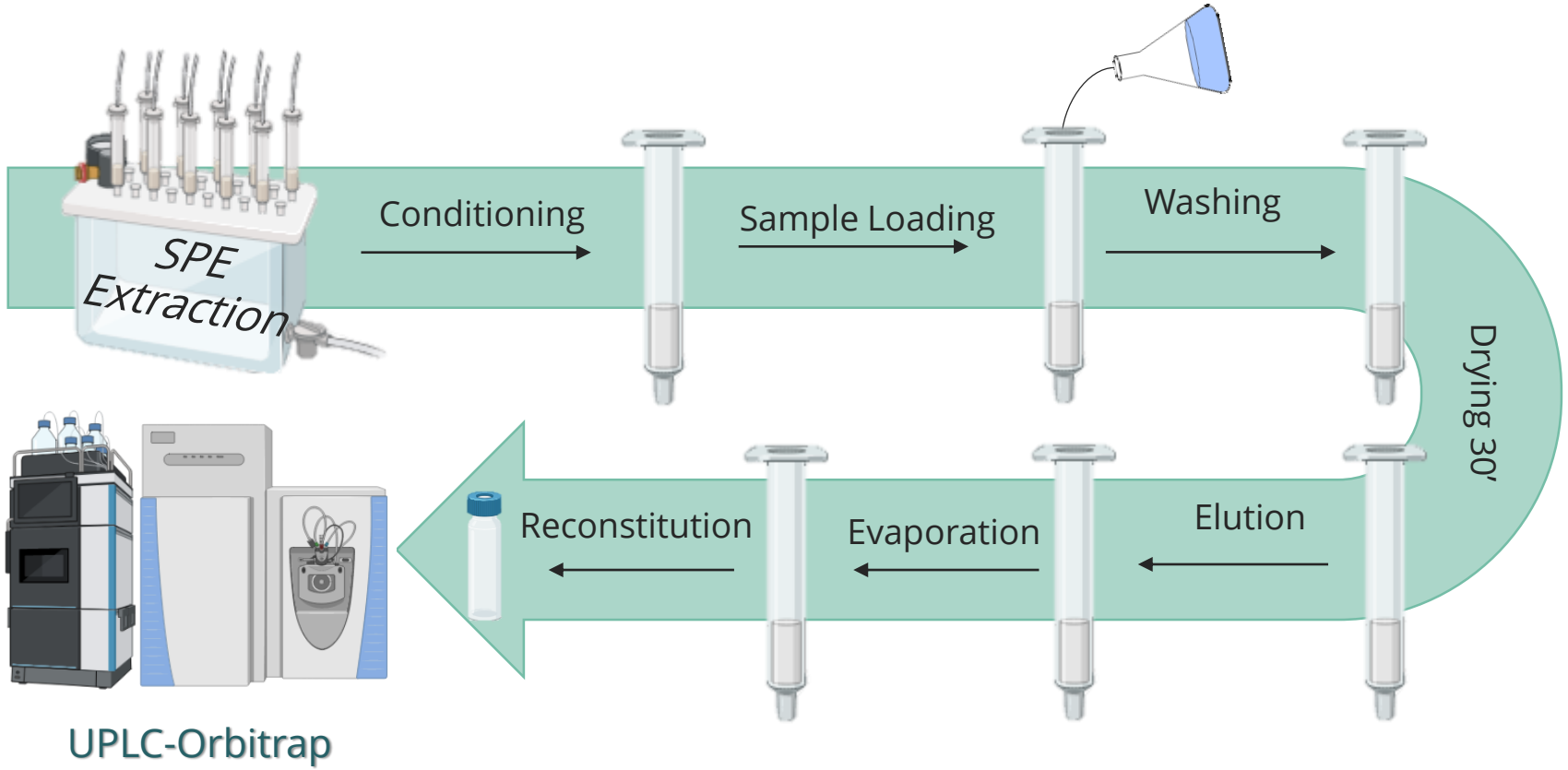


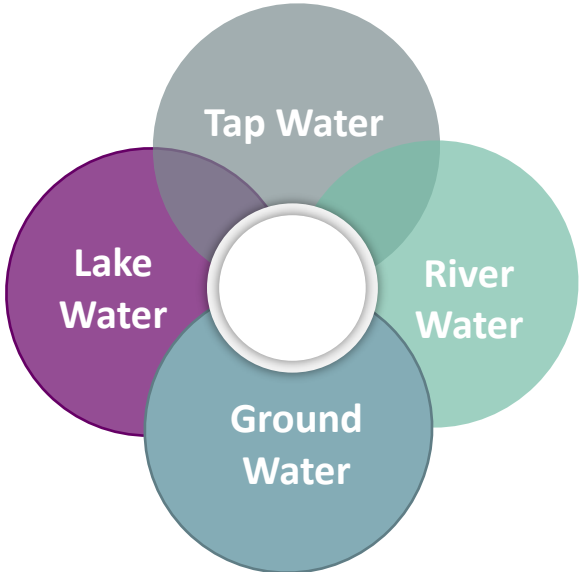
Real Sample Analysis

Pesticides,
Pharmaceuticals,
PCPs,
Industrial Chemicals

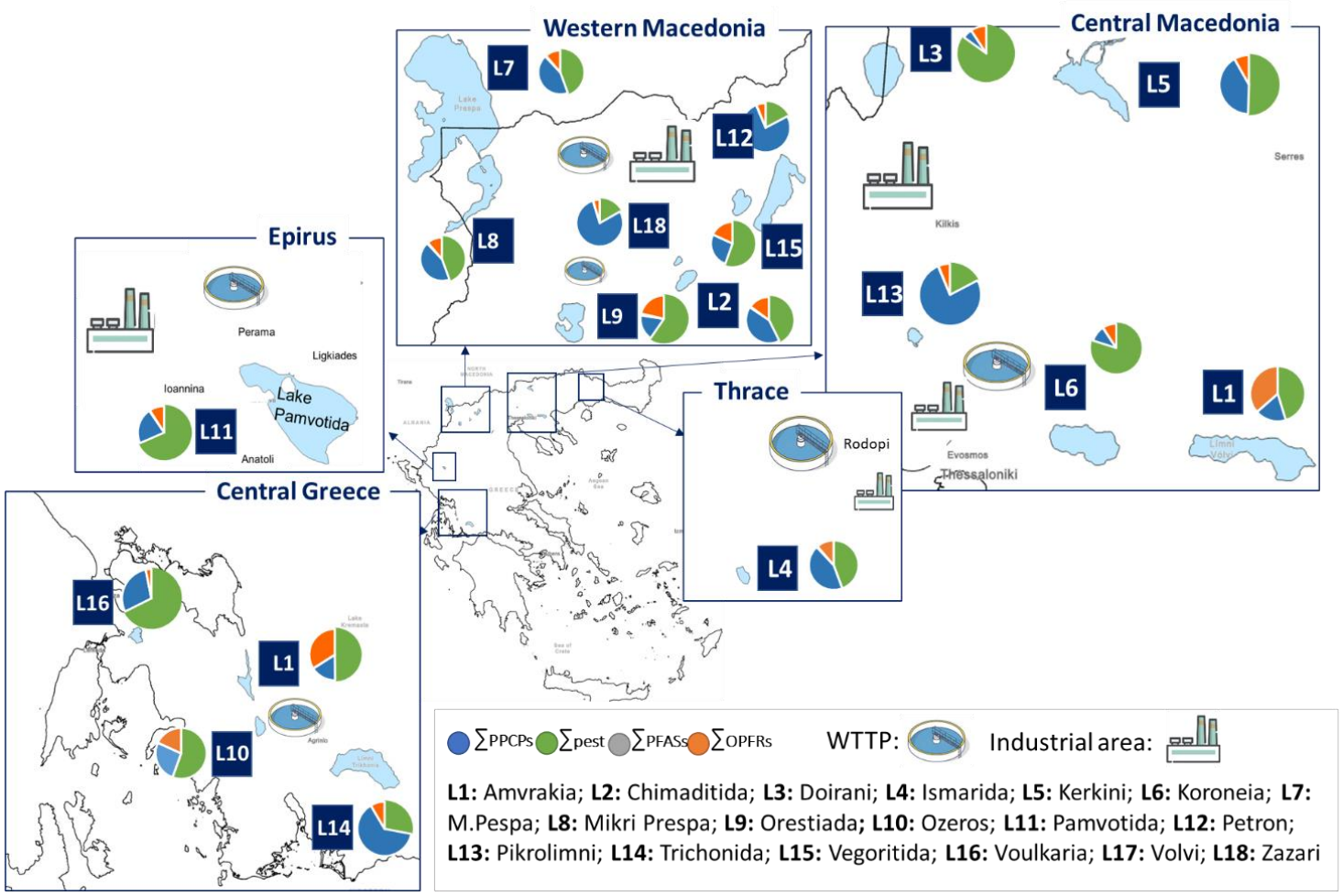
PFAS

Real Samples





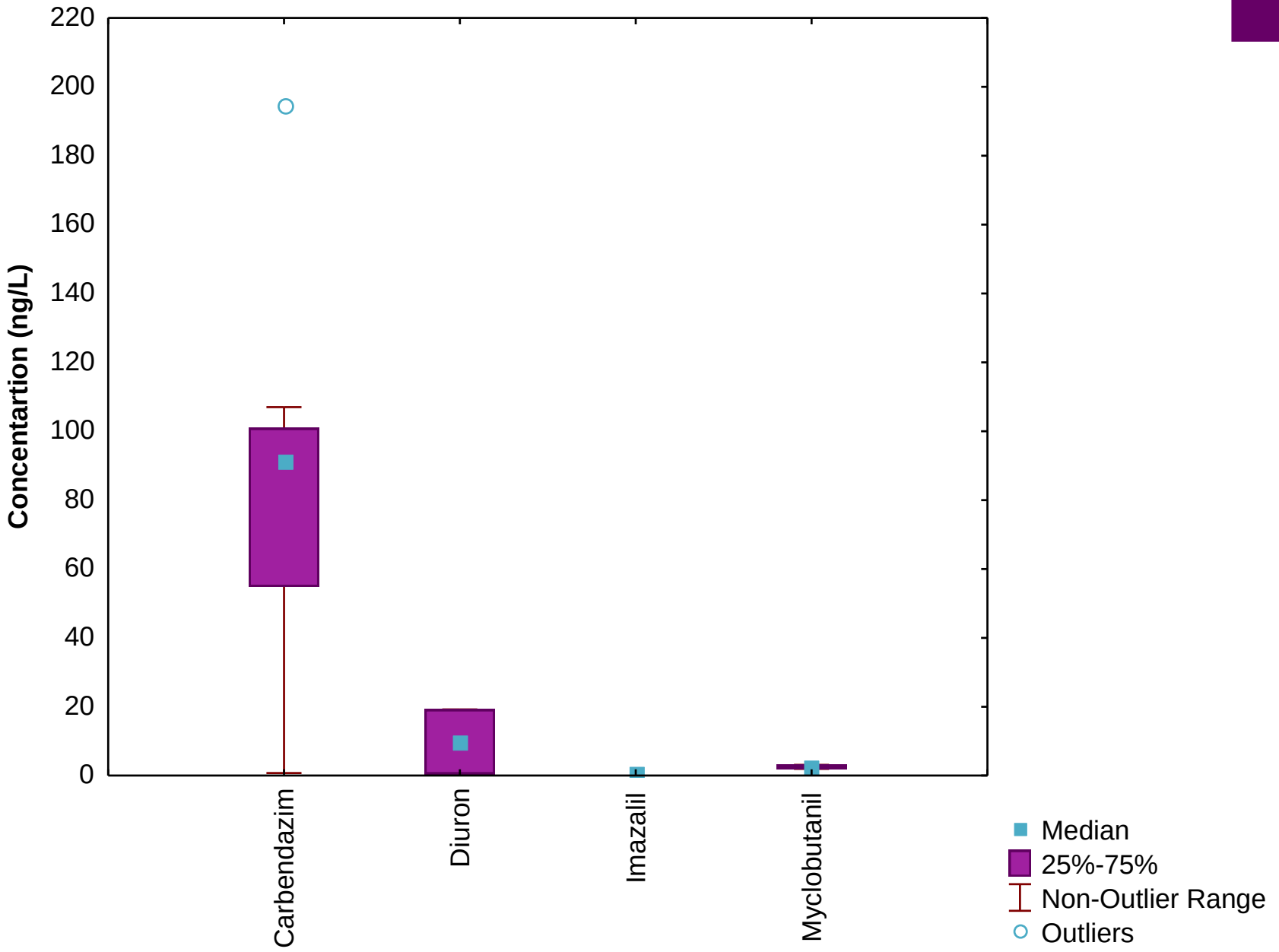
Real Samples



Lake Water

Real Samples

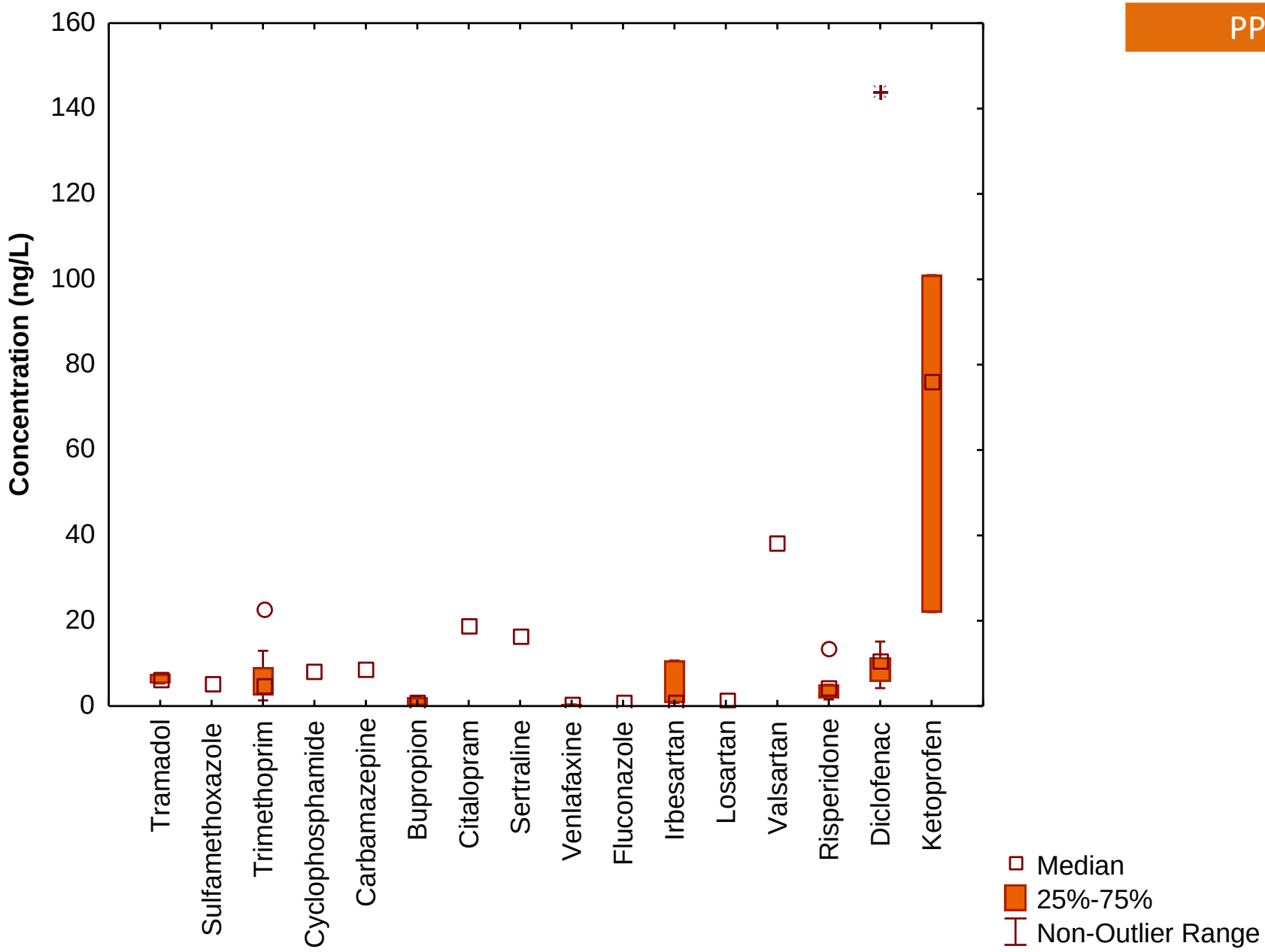
Pesticides



Lake Water

Real Samples

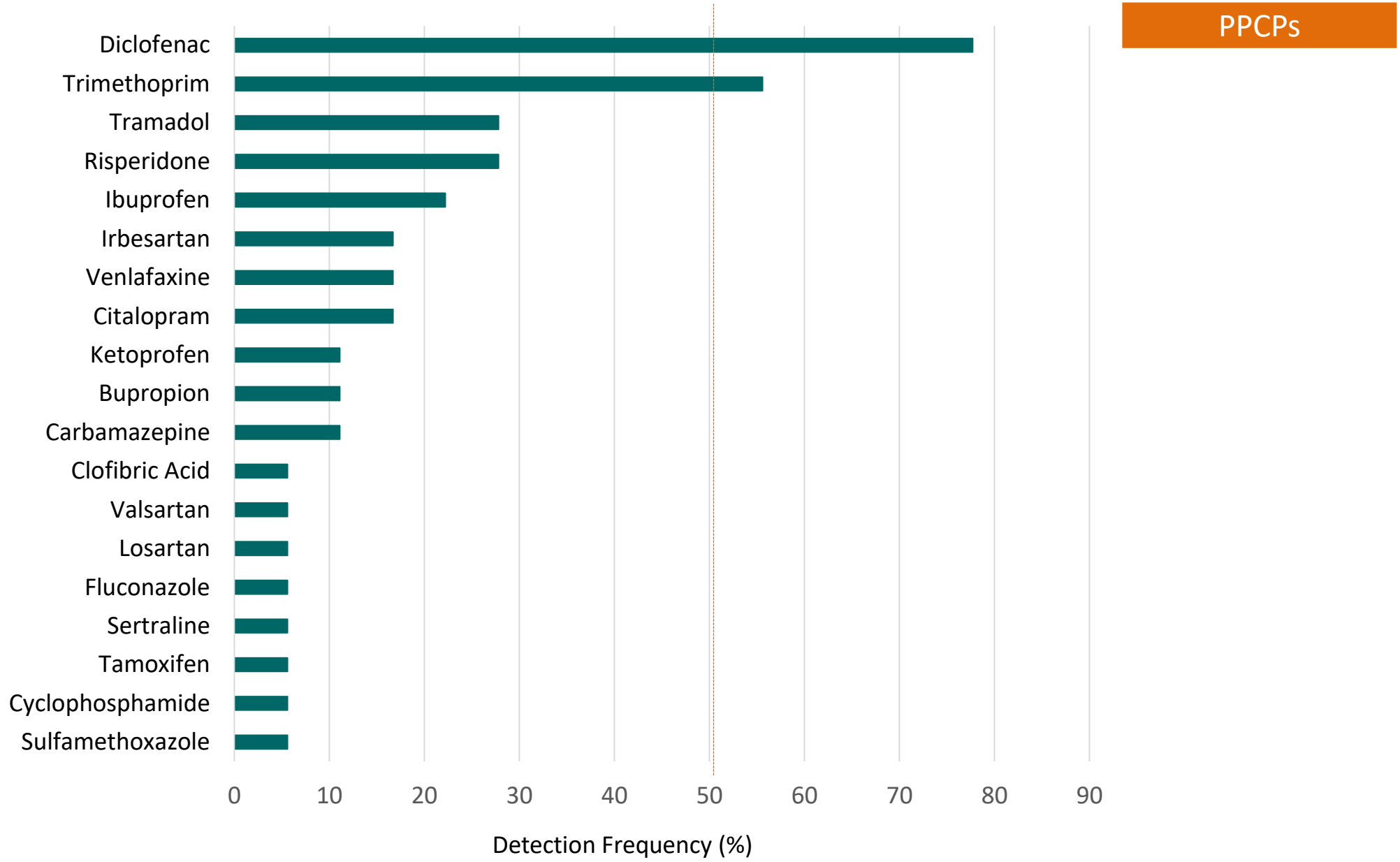
PPCPs



Lake Water

Real Samples

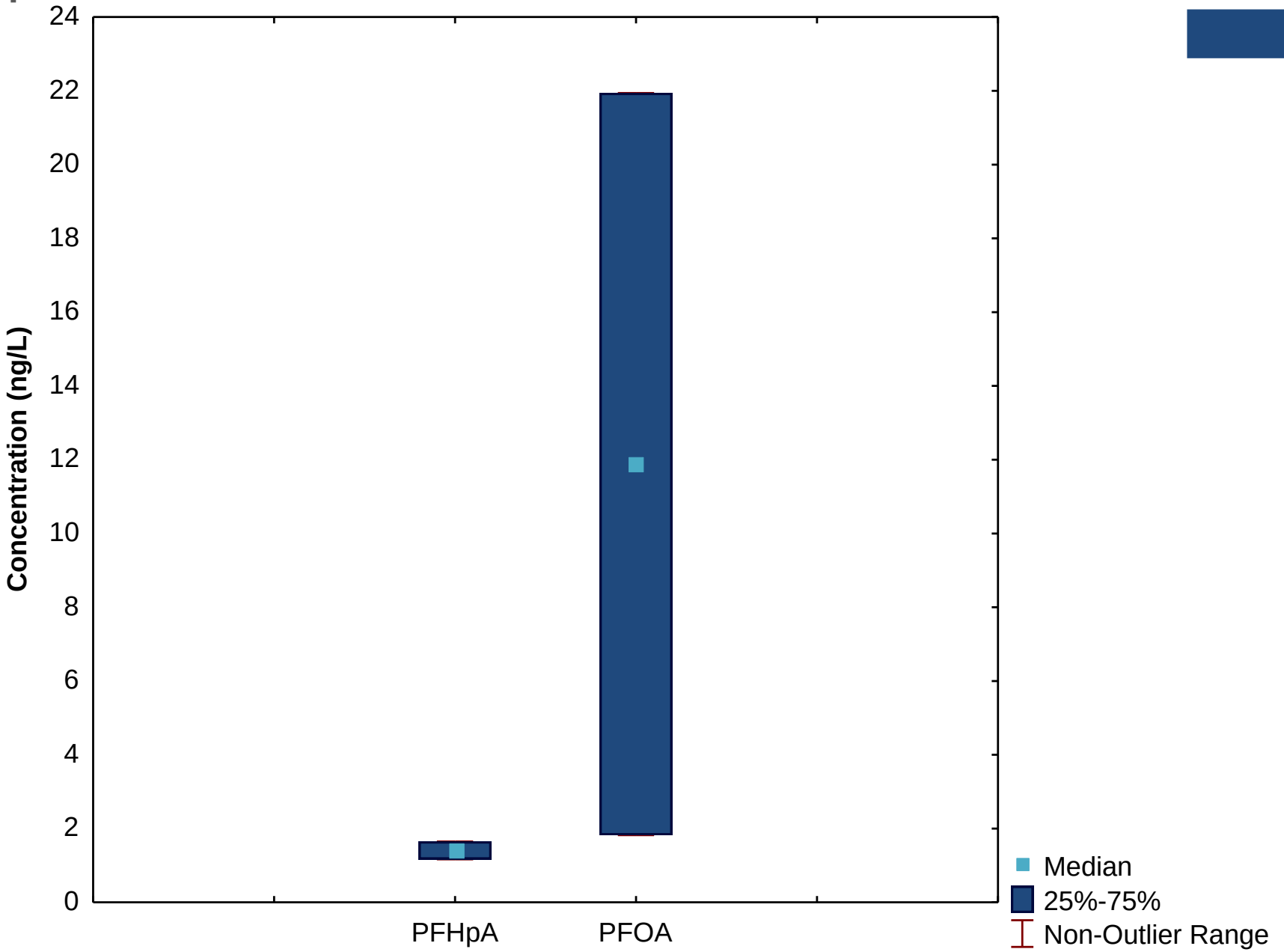
PPCPs



Lake Water

Real Samples

PFAS

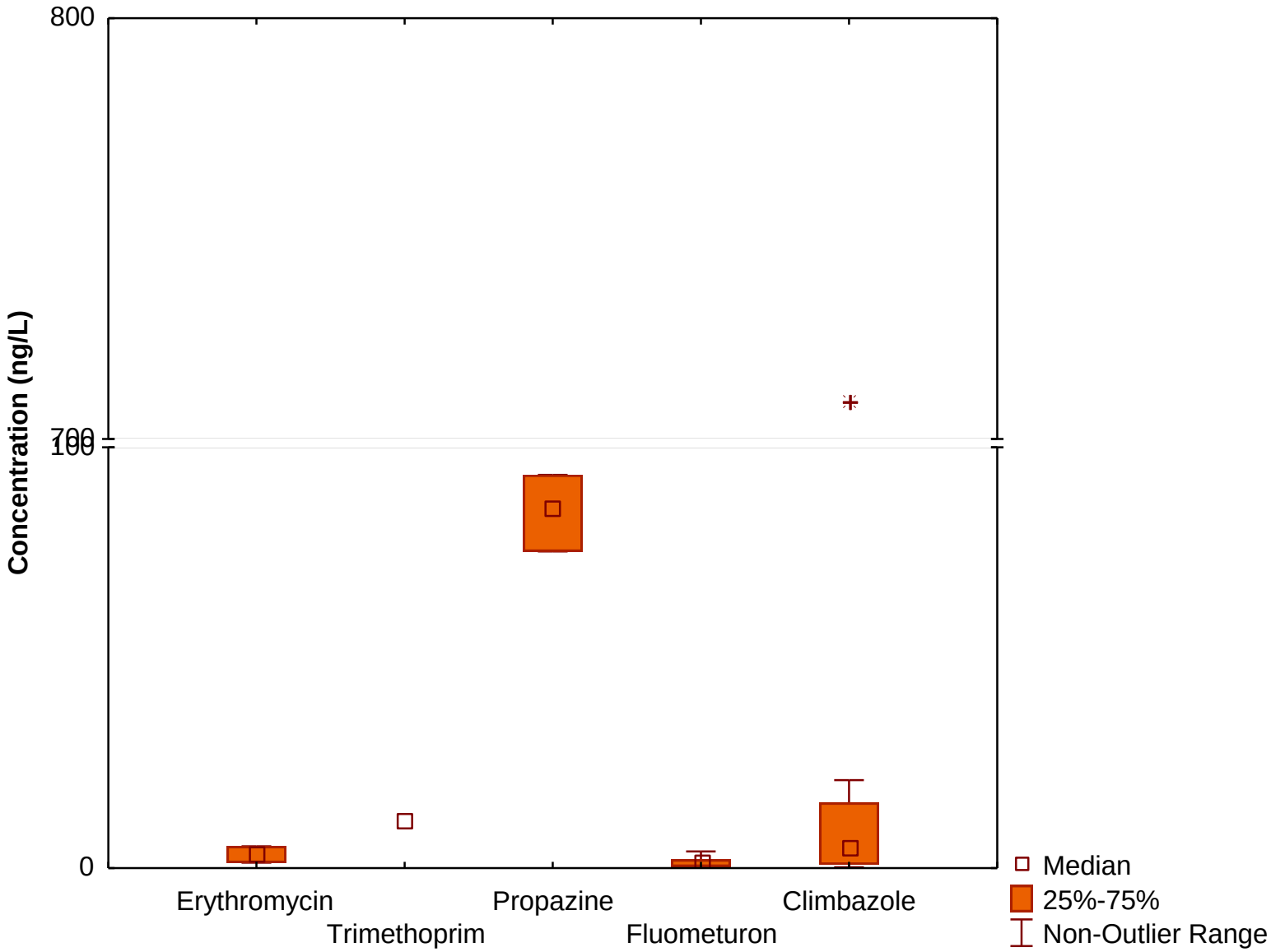


Lake Water

Real Samples

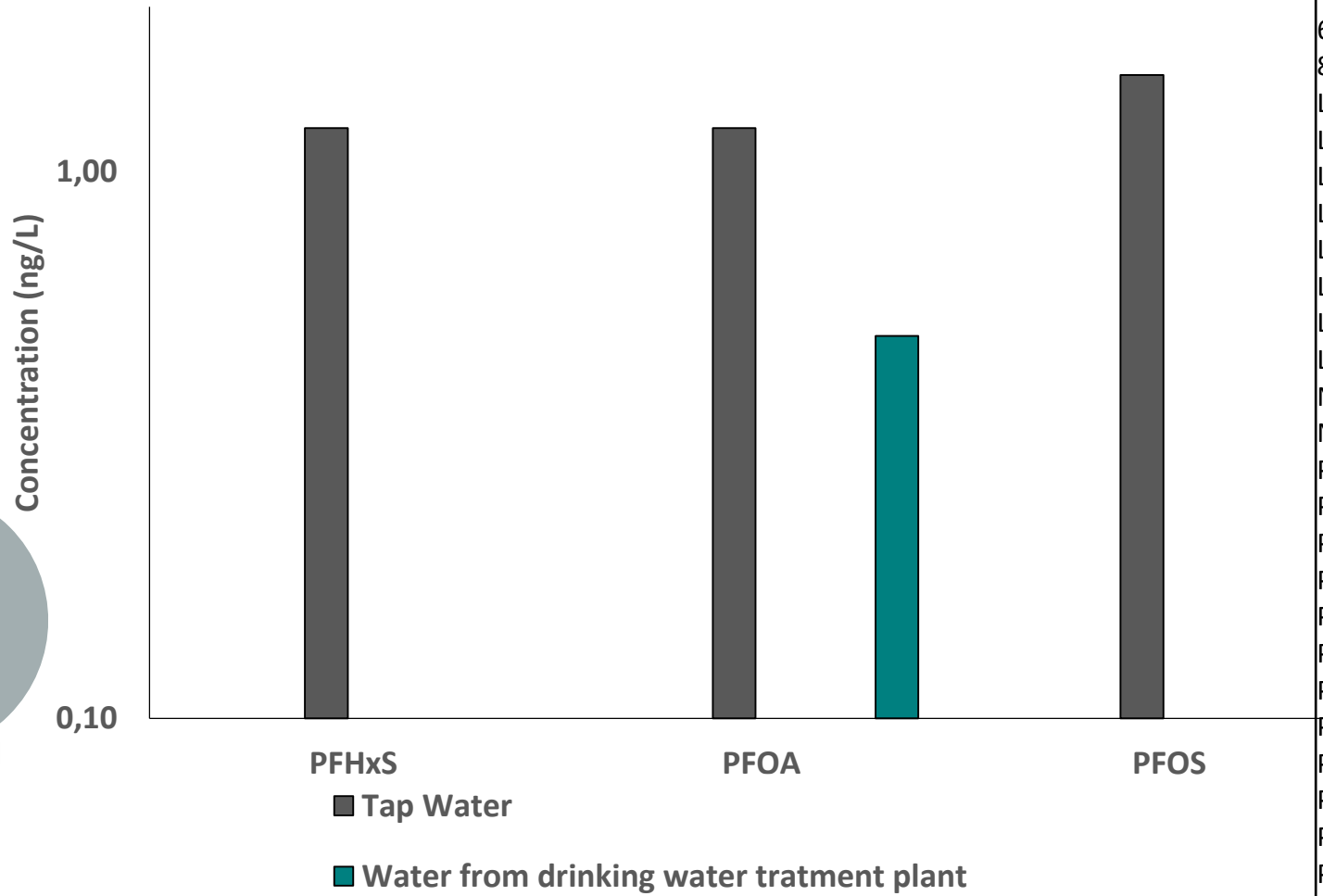
All ECs

Tap Water



Real Samples

Tap Water

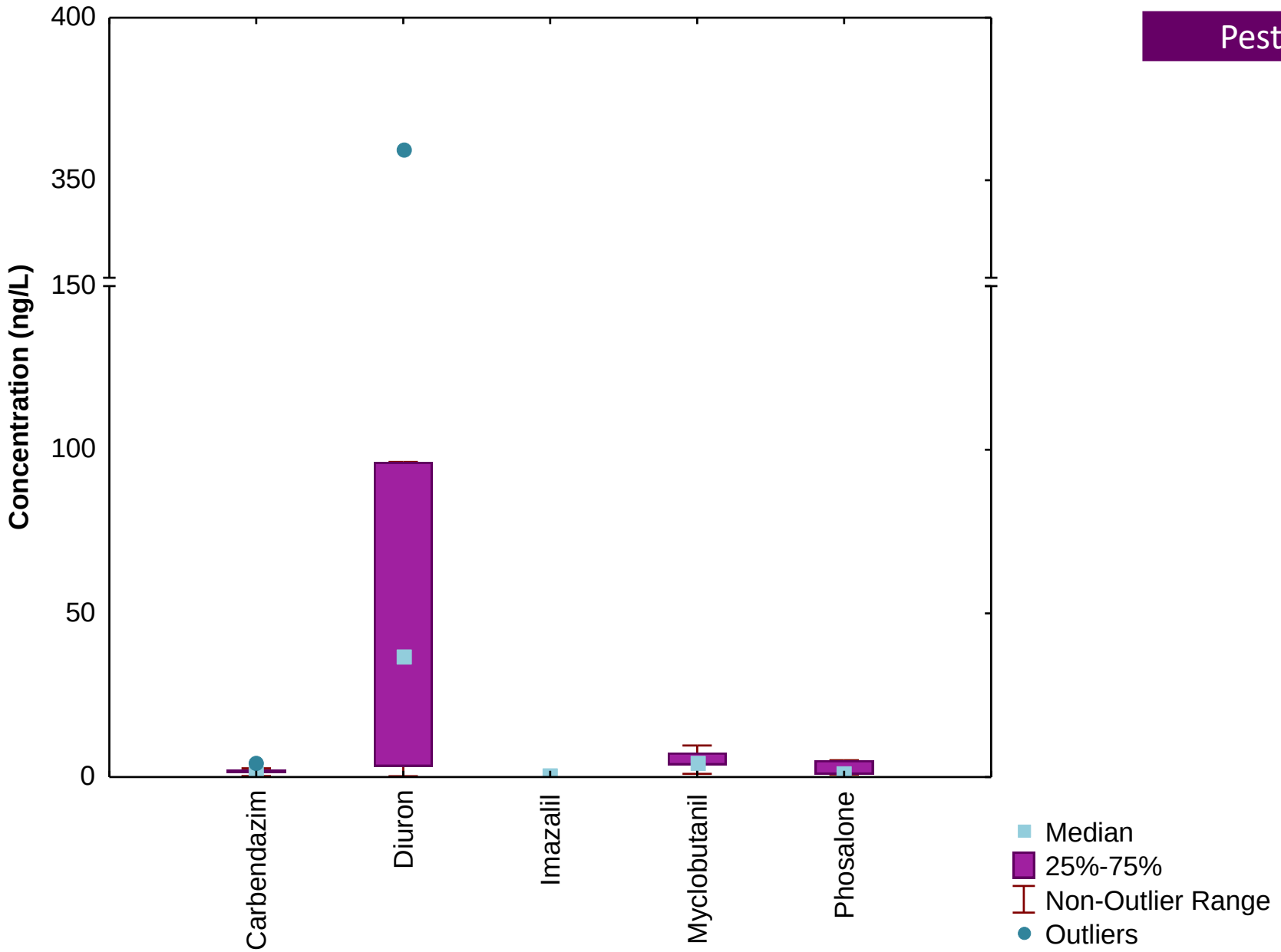


PFAS

Compound	MDL (ng L^{-1})	MQL (ng L^{-1})
4:2FtS	0.0004	0.0014
6:2FtS	0.0133	0.0438
8:2FtS	0.0003	0.0011
L-PFBS	0.0016	0.0054
L-PFDoS	0.0625	0.2063
L-PFDS	0.0027	0.0090
L-PFHpS	0.0018	0.0061
L-PFNS	0.0017	0.0055
L-PFPeS	0.0173	0.0572
L-PFTrDS	0.0188	0.0619
L-PFUdS	0.0370	0.1222
N-EtFOSAA	0.0068	0.0225
N-MeFOSAA	0.0548	0.1810
PFBA	0.0128	0.0421
PFDA	0.0028	0.0094
PFDoA	0.0067	0.0221
PFHpA	0.0007	0.0024
PFHxA	0.0051	0.0167
PFHxS	0.0119	0.0393
PFNA	0.0151	0.0497
PFOA	0.0123	0.0406
PFOS	0.0240	0.0792
PFOSA	0.0024	0.0078
PFPeA	0.0789	0.2605
PFTeDA	0.0138	0.0454
PFTrDA	0.0084	0.0276
PFUdA	0.0056	0.0185

Real Samples

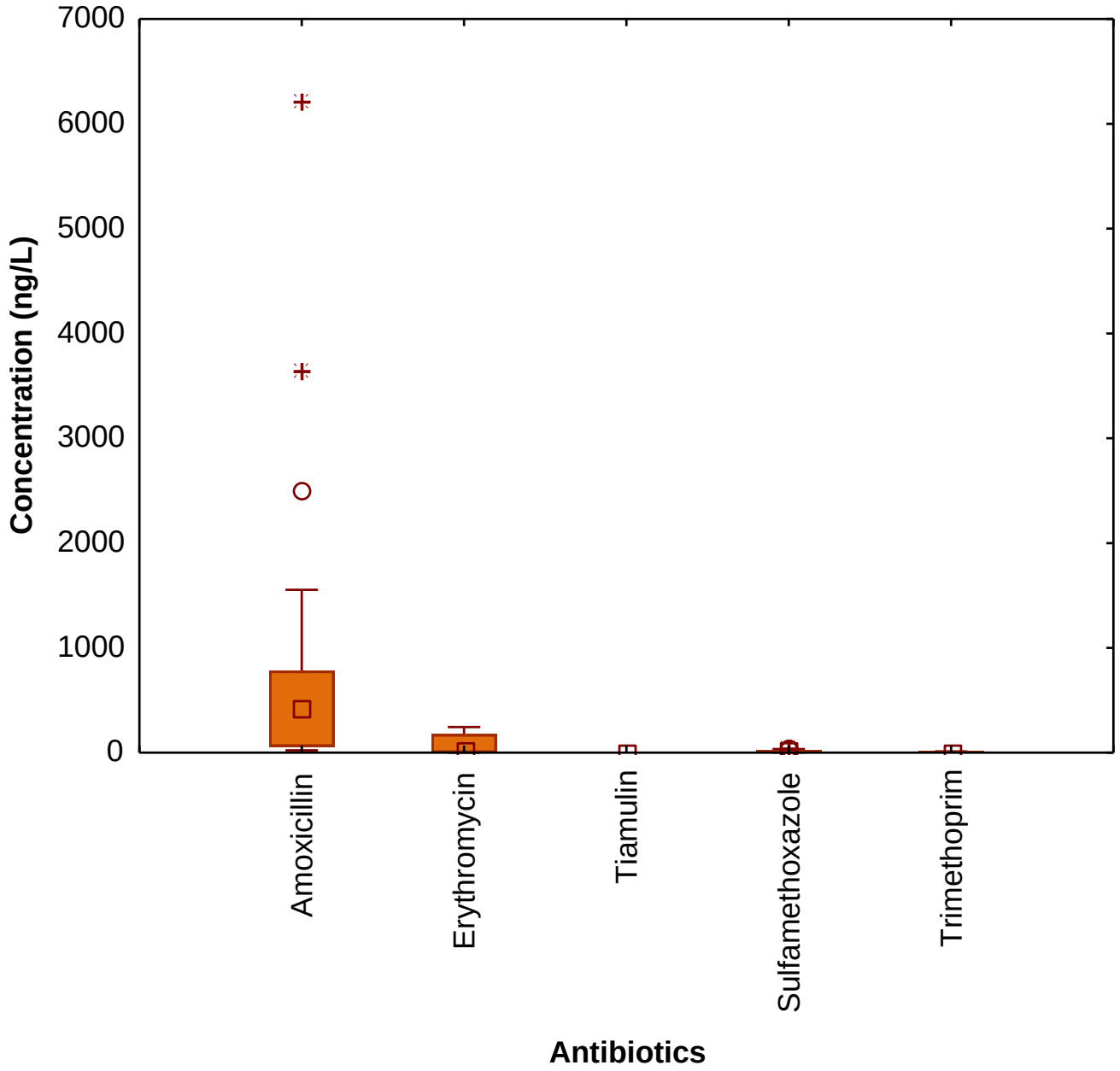
Pesticides



River Water

Real Samples

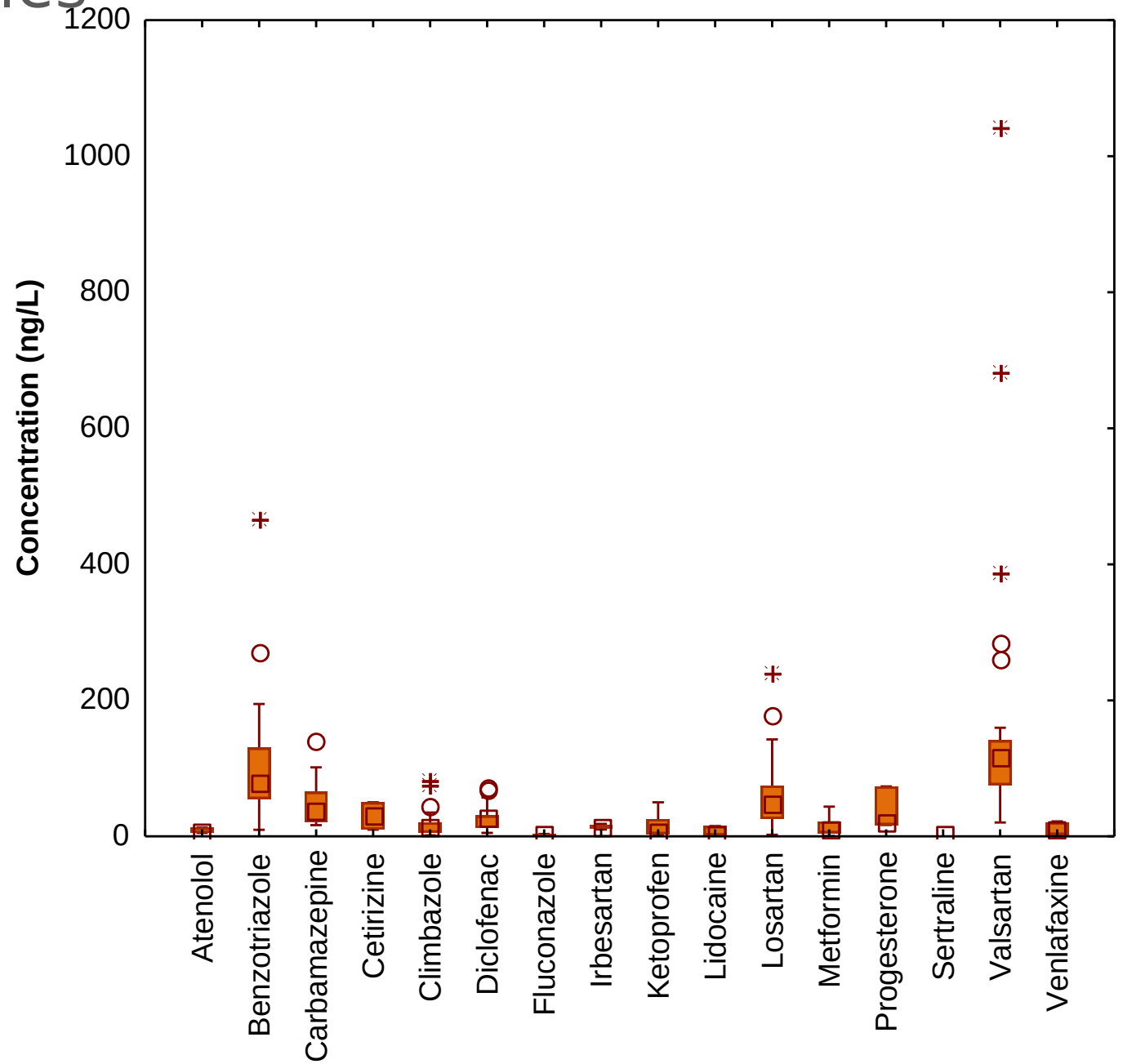
Antibiotics



River Water

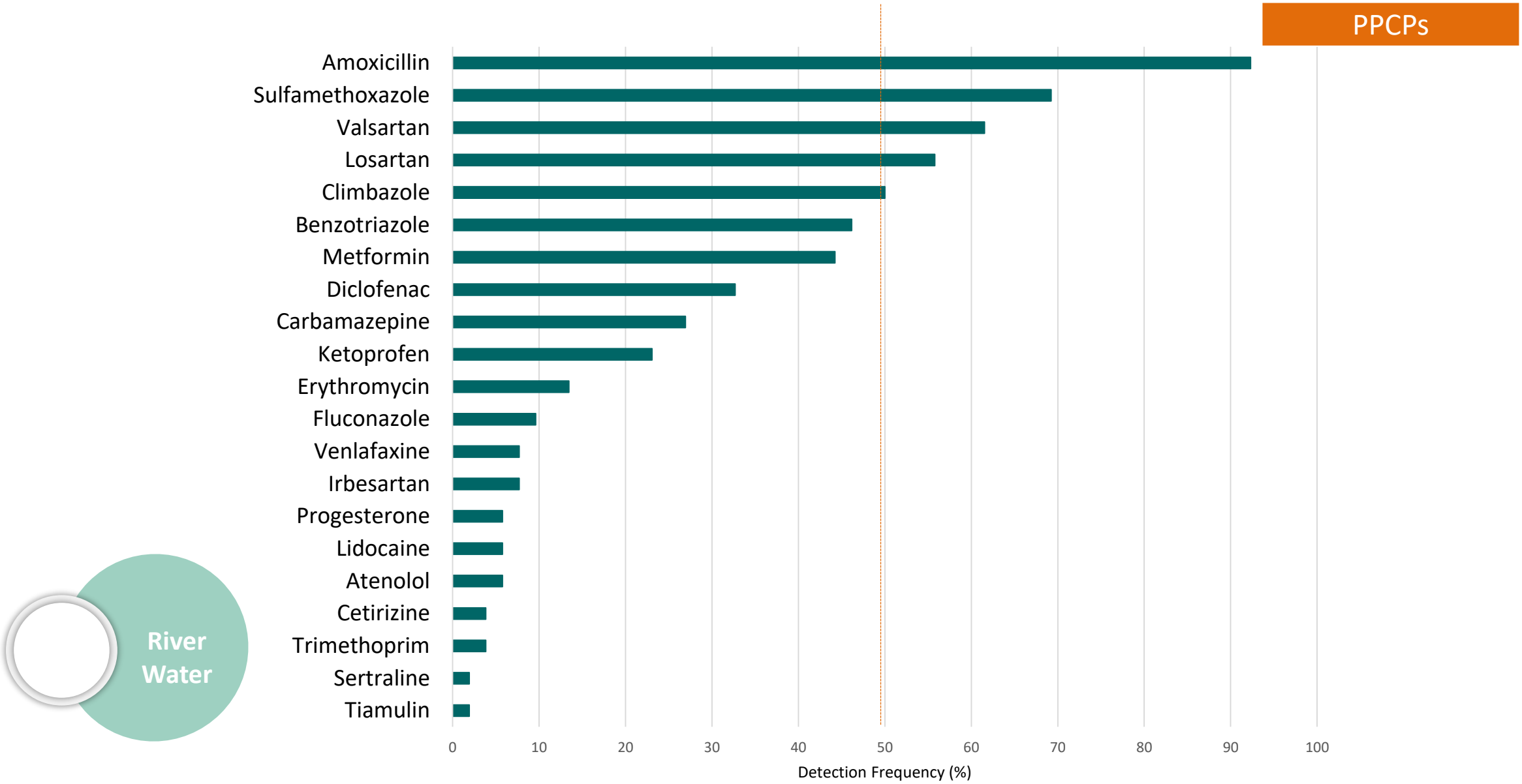
Real Samples

PPCPs



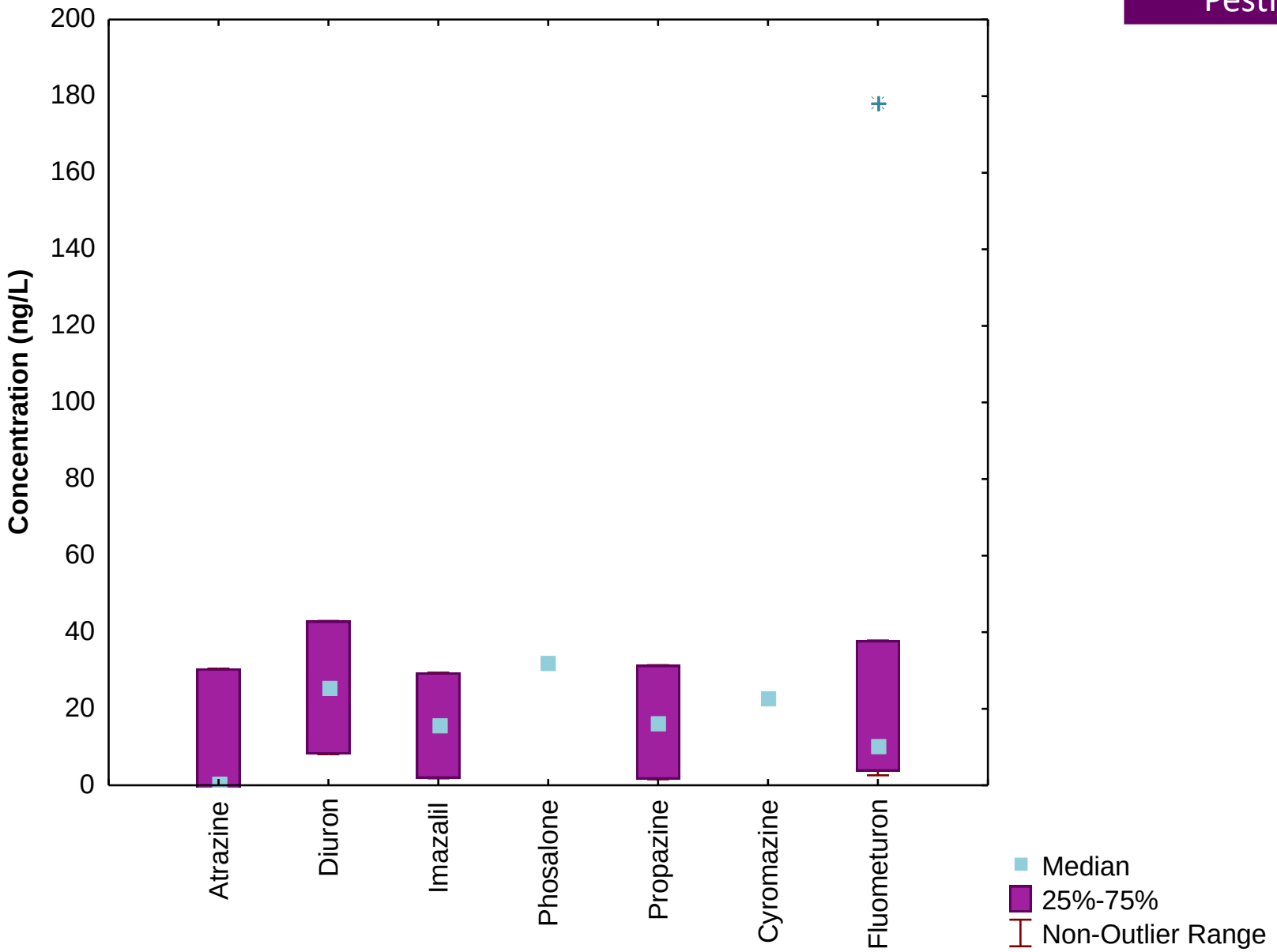
River Water

Real Samples



Real Samples

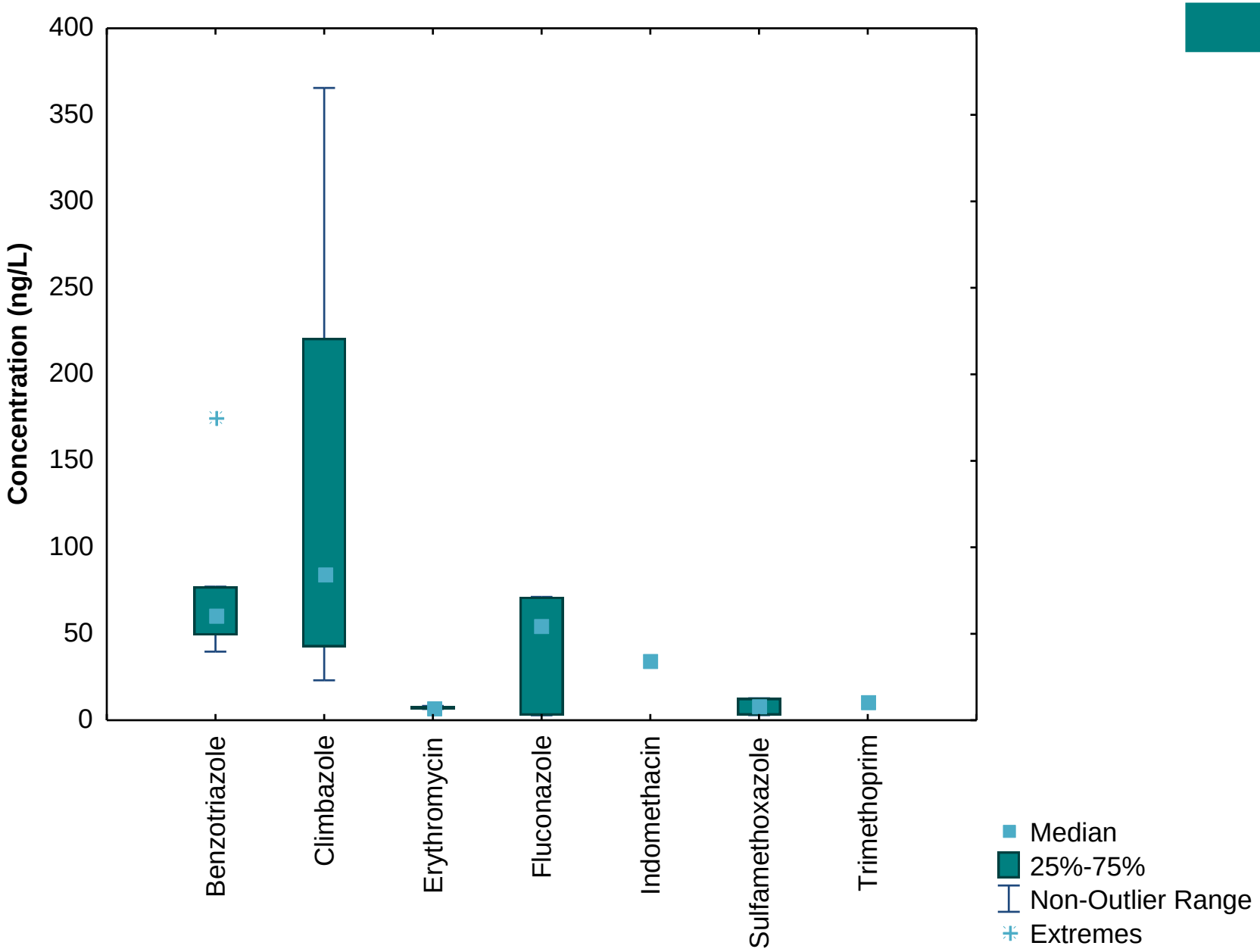
Pesticides



Ground Water

Real Samples

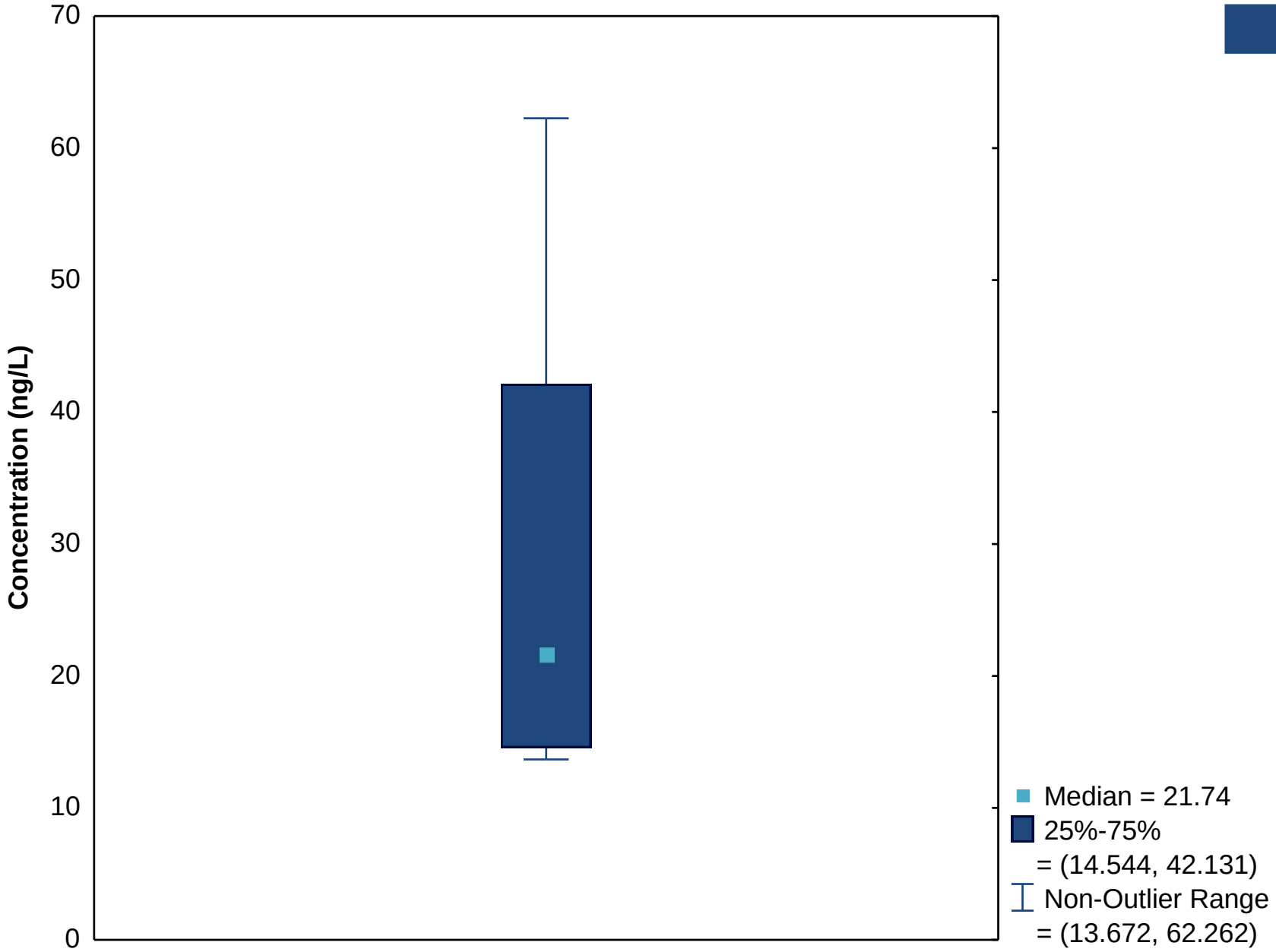
PPCPs



Ground Water

Real Samples

PFAS



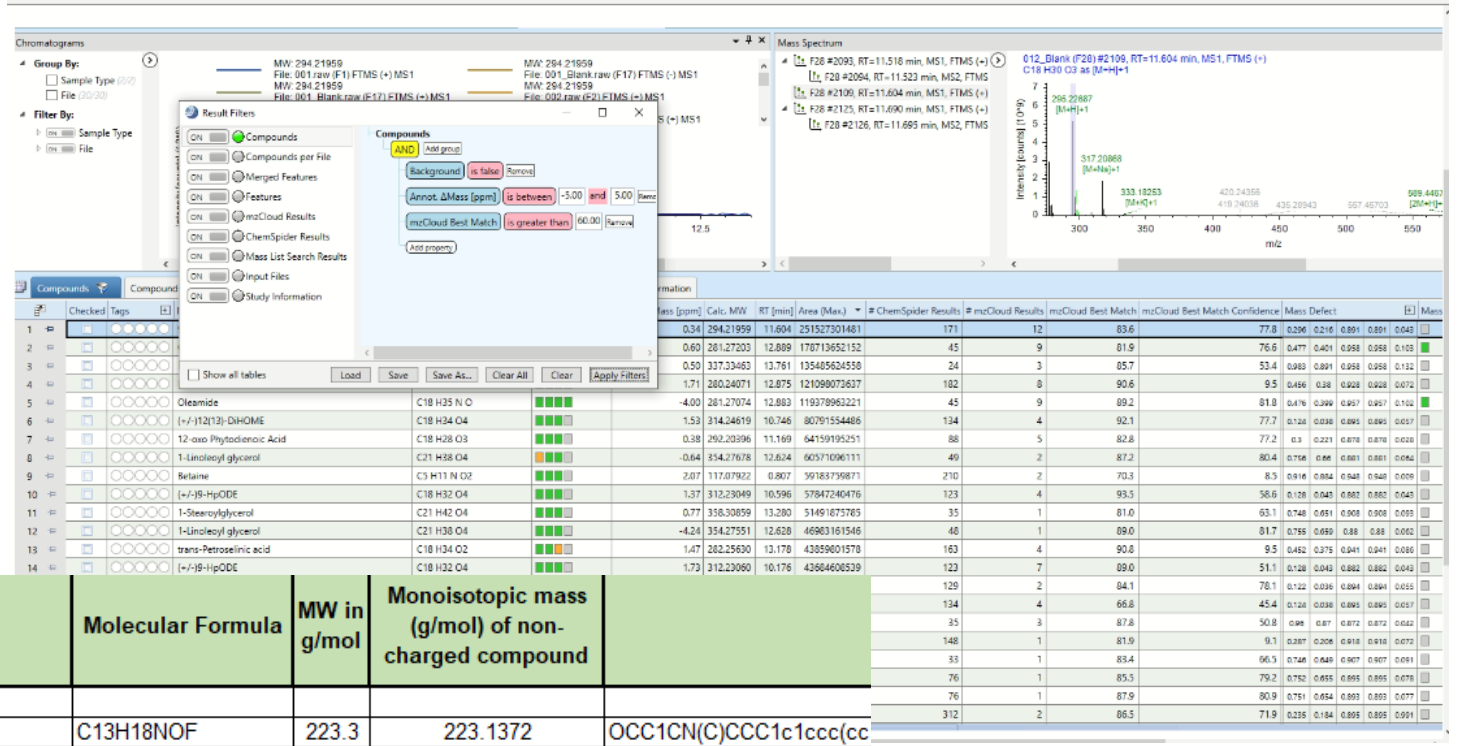
Ground Water

Real Samples

On going

Future Remarks

Suspect Screening



CAS	Substance Name	Molecular Formula	MW in g/mol	Monoisotopic mass (g/mol) of non-charged compound	
149-64-4	(-)-Scopolamine-N-butyl				
105812-81-5	(-)-trans-4-(4'-fluorophenyl)-3-hydroxymethyl-N-methylpiperidine	C13H18NOF	223.3	223.1372	OCC1CN(C)CCC1c1ccc(cc
	(+)-menthol	C10H20O		156.1514153	CC(C)C1CCC(C)CC1O
107898-54-4	(+/-) trans-3,3-dimethyl-5-(2,2,3-trimethyl-cyclopent-3-en-1-yl)pent-4-en-2-ol	C15H26O	222.4	222.1984	CC(C(C=CC1CC=C(C1(C)C
	(1,4-diazabicyclo[2.2.2]octane-2-yl)methanol	C7H14N2O		142.1106131	N12C(CO)CN(CC1)CC2
	(13Z)-Docos-13-enoic acid	C22H42O2		338.3184806	CCCCCCCC/C=C\CCCCCC
342573-75-5	(1-Ethyl-3-methylimidazolium) ethyl sulfate	C2H5O4S	126.1	124.9909	CCOS(=O)(=O)[O-]
	(1-Hydroxycyclohexyl)(phenyl)methanone	C13H16O2		204.1150298	OC1(CCCCC1)C(=O)c1ccc
42978-66-5	(1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] diacrylate	C15H24O6	300.4	300.1573	C=CC(=O)OCC(OCC(OCC(
82203-23-4	(1R)-1-[(4R,4aR,8aS)-2,6-bis(4-chlorophenyl)tetrahydro[1,3]dioxino[5,4-d][1,3]dioxin-4-yl	C20H20O6Cl2	427.3	426.0637	OCC(C1OC(OC2C1OC(OC2
521284-22-0	(1R)-2-{[2-(4-aminophenyl)ethyl]amino}-1-phenylethanol hydrochloride	C16H20N2O	256.3	256.1576	Nc1ccc(cc1)CCNC[C@@H
119302-24-8	(1R,2R,4R,5S,7S,10R,11R,13R,14R,15S)-5-hydroxy-2,15-dimethyl-4-(morpholin-4-yl)-13	C29H48N2O4	488.7	488.3614	CC(=O)OC1C(CC2C1(C)CC
188199-50-0	(1R,2S,2'S,4R)-1,7,7-Trimethylbicyclo (2.2.1)heptane-2-spiro-4'-(2''-isopropyl-1'',3''-dioxan	C16H28O2	252.4	252.2089	CC([C@@H]1OCC[C@@]2
847565-09-7	(1R,2S,5R)-5-methyl-2-(propan-2-yl)-N-[2-(pyridin-2-yl)ethyl]cyclohexanecarboxamide	C18H28N2O	288.4	288.2202	CC1CCC(C(C1)C(=O)NCCc
172015-79-1	(1S-cis)-4-(2-amino-6-chloro-9H-purin-9-yl)-2-cyclopentene-1-methanol hydrochloride	C11H12N5OCl	265.7	265.0730	OC[C@@H]1C=C[C@@H]

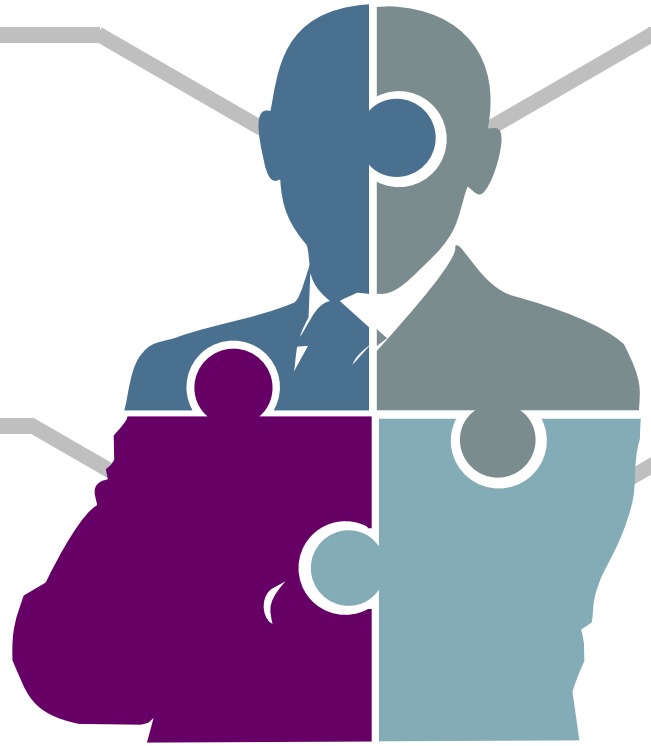
CONCLUSIONS

Conclusions

Analytical method

Determine as much (non) PM as possible

PM substances do not have lower likelihood of detection than a non PM register substance



PM/ non PM

PM list should be revised

Future –Suspect Screening

Comprehensive monitoring


Portorož
thank you
Thessaloniki

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High-Resolution Mass Spec

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