Anyone for a cocktail? A brief look at the chemicals entering our surface waters

Fiona Regan, School of Chemical Sciences, Dublin City University, DCU Water Institute

Dublin Urban Rivers LIFE Project

Water Quality in Urban Rivers Conference

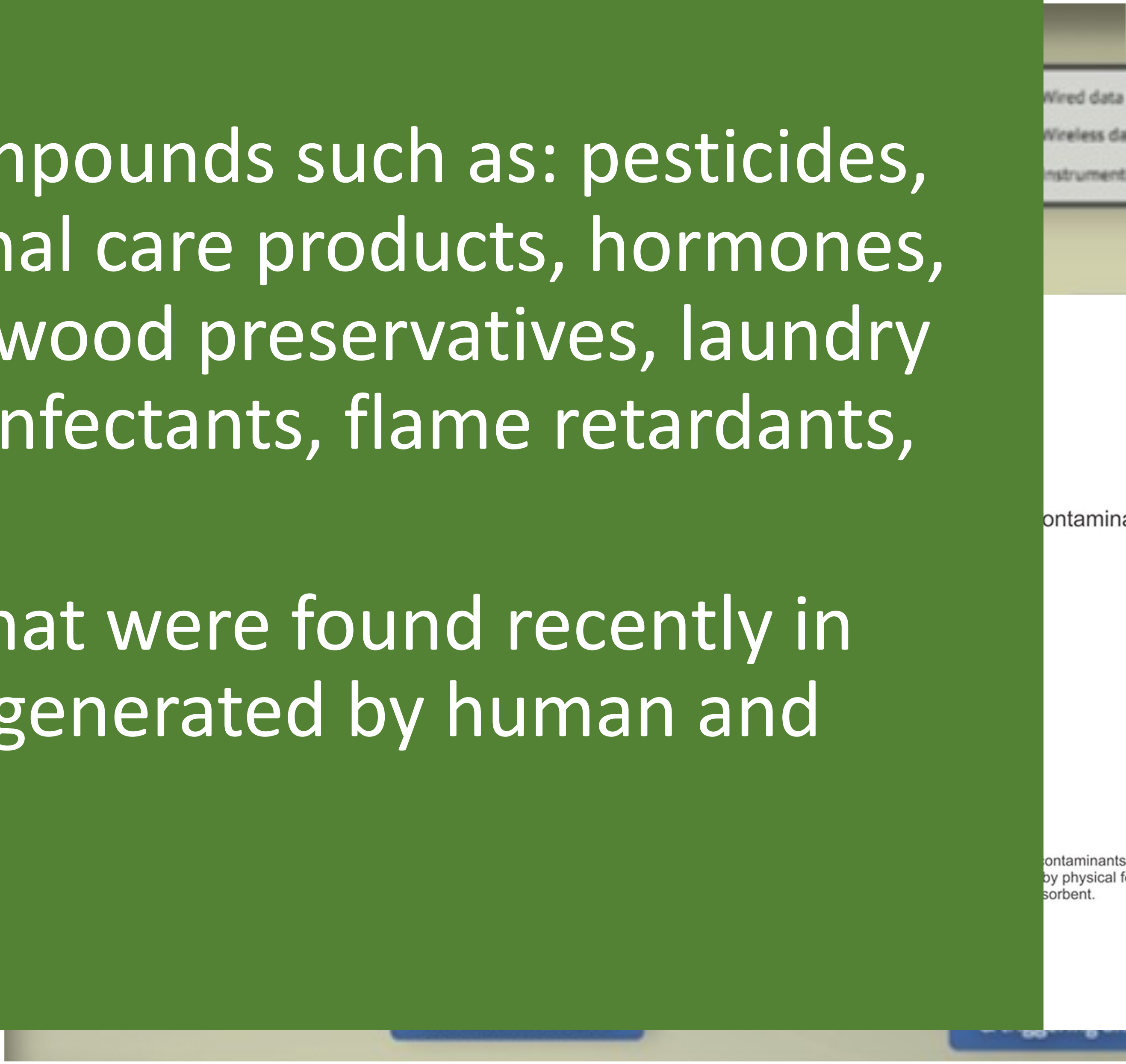
28th May 2024

Outline

- The emerging challenges and policy landscape
- Chemical cocktails –
- Monitoring – Data from studies
- Effects and risk assessment

Challenge- Emerging contaminants

- Emerging contaminants (EC's) are pollutants of growing concern.
- They are mainly organic compounds such as: pesticides, pharmaceuticals and personal care products, hormones, plasticizers, food additives, wood preservatives, laundry detergents, surfactants, disinfectants, flame retardants, and
- other organic compounds that were found recently in natural wastewater stream generated by human and industrial activities.



Towards an improved risk assessment framework

…design of better chemicals,

Chemical pollution can have long-term and large-scale environmental impacts

The new term “toxic-free environment” is considered, by some, to be political, while for others, the phrase might appear non scientific as, in the end, everything can be toxic depending on the dose or concentration.

Inconsistent risk assessments can create public mistrust, as with glyphosate and bisphenol-A

The zero pollution ambition for a toxic-free environment implies a continuous improvement of the environmental status;
Currently risk assessments do not predict the impact of a chemical, especially a persistent one, in years from now by continued emission.

Additional Water treatment requirements

- EU law – Urban Wastewater Treatment Directive → removal of micropollutants
- Adding a 4th level of treatment
- Ireland must improve compliance – currently at 51% of current standards whereas EU average is 90%

Chemical Cocktail

Chemical cocktails harmful to wildlife found in 81% of English rivers and lakes

Campaigners call for rigorous testing of waterways to protect species

after analysis reveals scale of problem

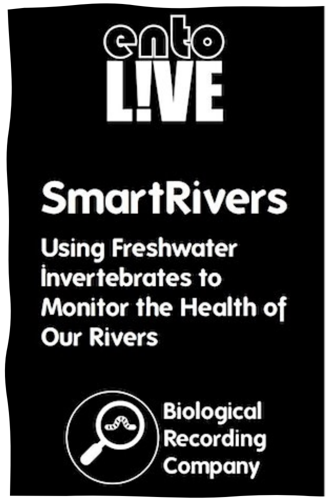
In Europe, the chemicals policy has evolved since the 1960s and has generated over 40 pieces of legislation.

all European policies on the environment should be based on the precautionary principle

the polluter should pay

risk assessment process should be harmonized.

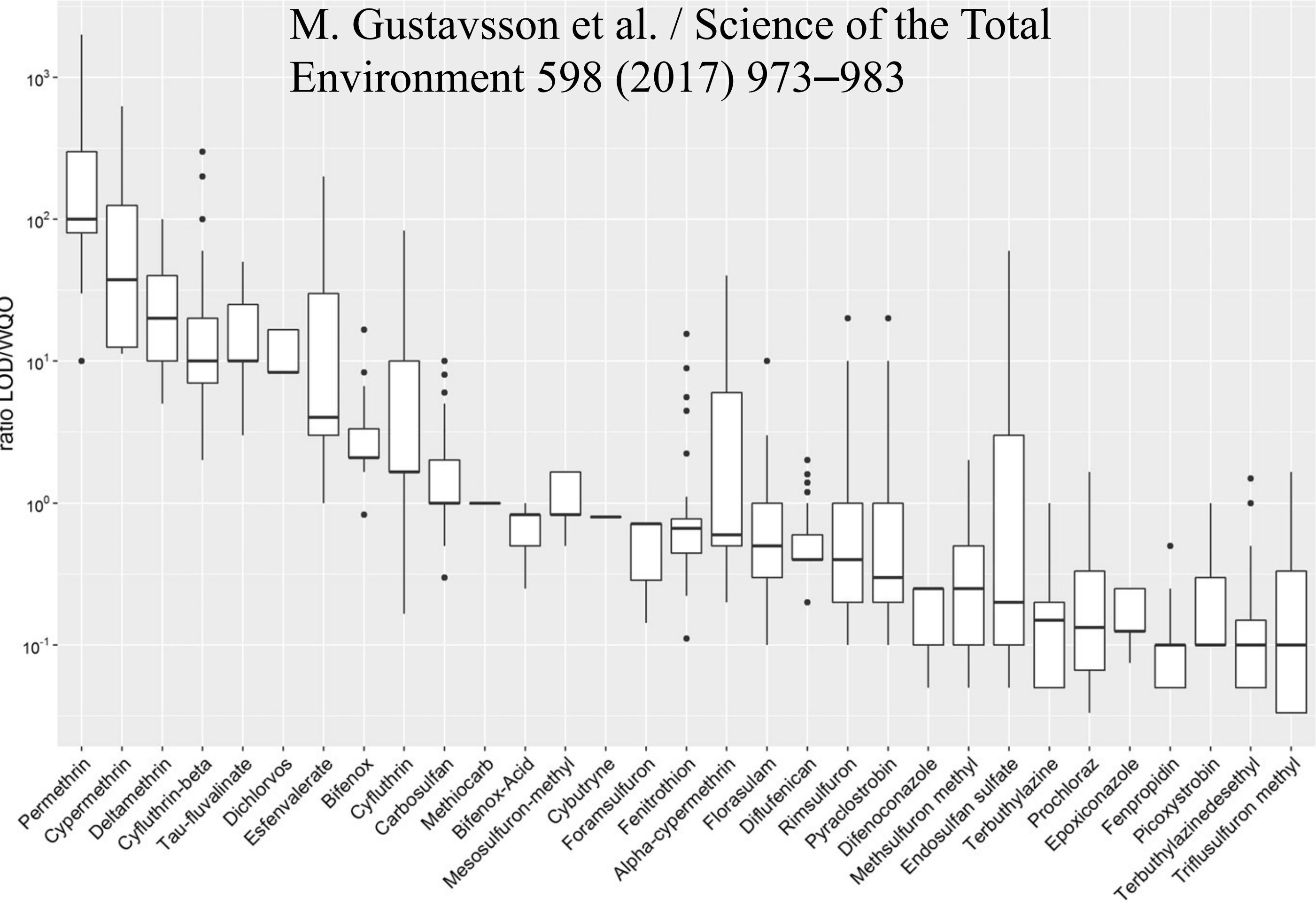
The EU tries to achieve this by enabling a “one substance–one assessment” approach.



Monitoring

- Matrix challenges

- Analytical methods



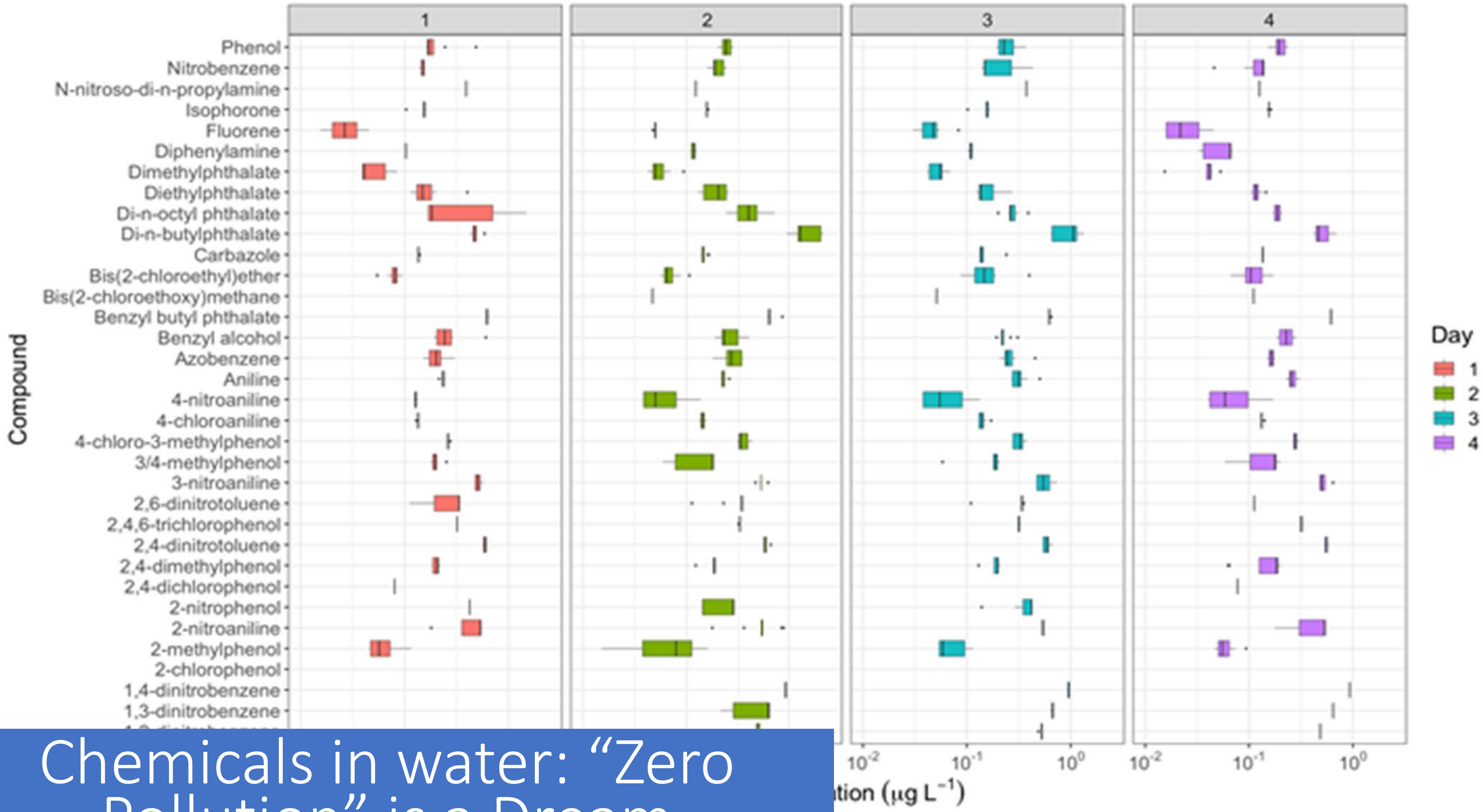
M. Gustavsson et al. / Science of the Total Environment 598 (2017) 973–983

Few studies have incorporated the analysis of the **metabolites of sulfonamide** in wastewater such as N_4-acetyl sulfamethoxazole and N_4-acetyl sulfamethazine.

metabolites - during wastewater treatment should be routinely considered ➔ known to be transformed back to the parent compounds in wastewater environments.

Significant complications in the quantification of antibiotics by liquid chromatography–mass spectrometry (LC–MS) →matrix-specific factors, vary depending on the origin and composition.

Surface water as an indicator



Chemicals in water: “Zero Pollution” is a Dream

Studies

Phthalate – occurrence and human exposures

PFAS – occurrence and potential sources

Pharmaceuticals – during and after COVID-19

Pesticides – in wastewater and surface water

Cycle of Phthalates and their Metabolites in the WWTP

Phthalates are ubiquitous synthetic organic compounds

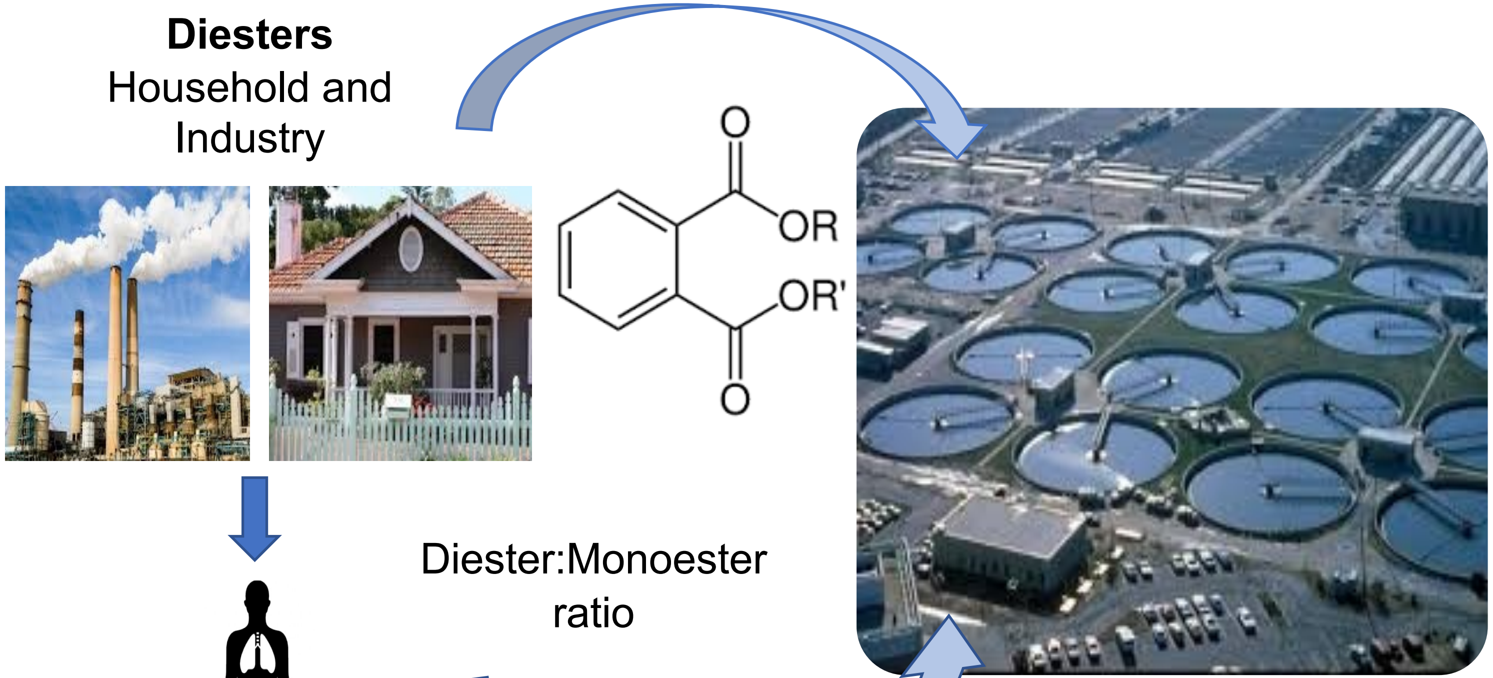
- Plasticisers
- Endocrine disruptors
- Banned/limited in manufacturing

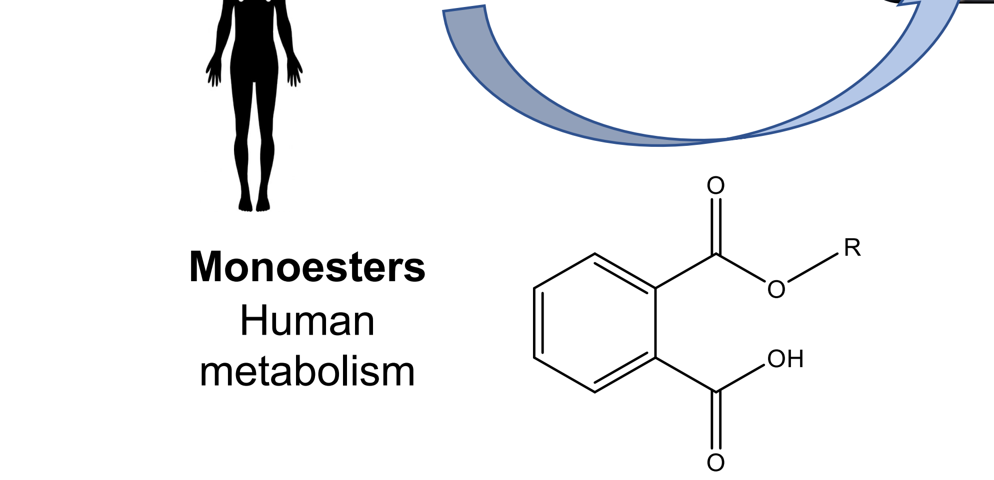
Exposure routes:

- Ingestion
- Inhalation
- Absorption

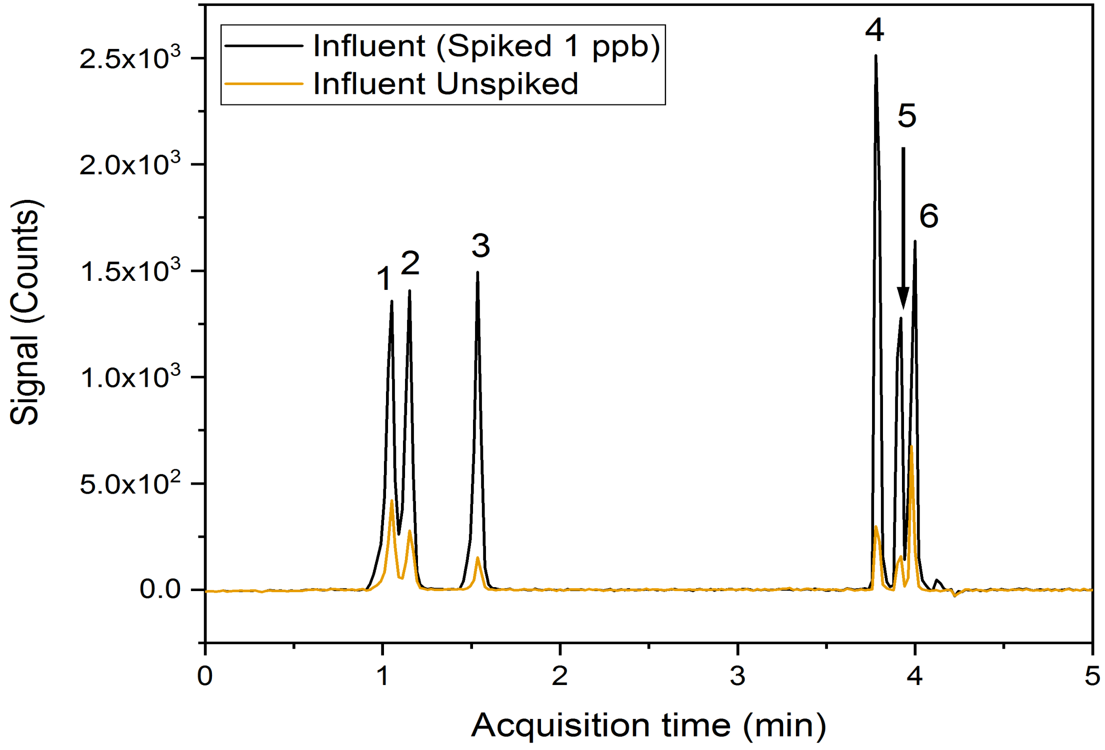
Health Impacts:

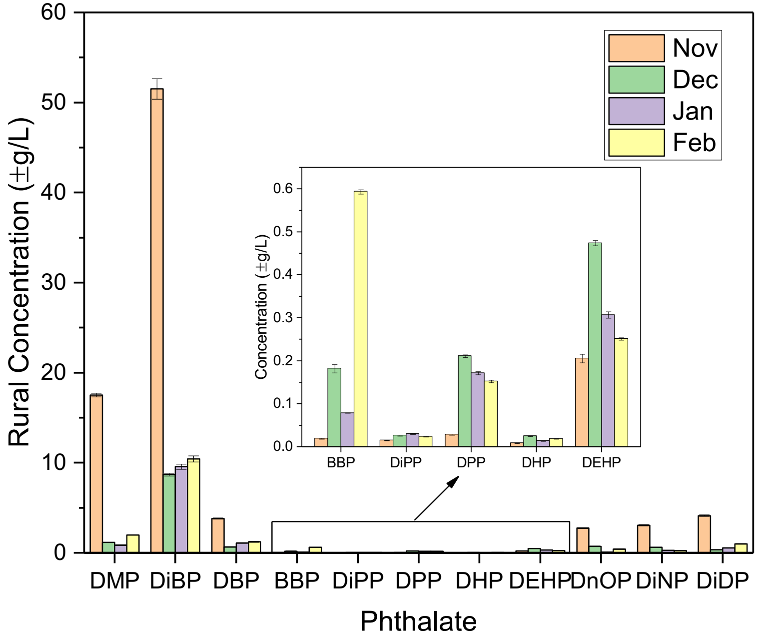
- Male Birth Defects
- Impaired neurological development in children
- Obesity

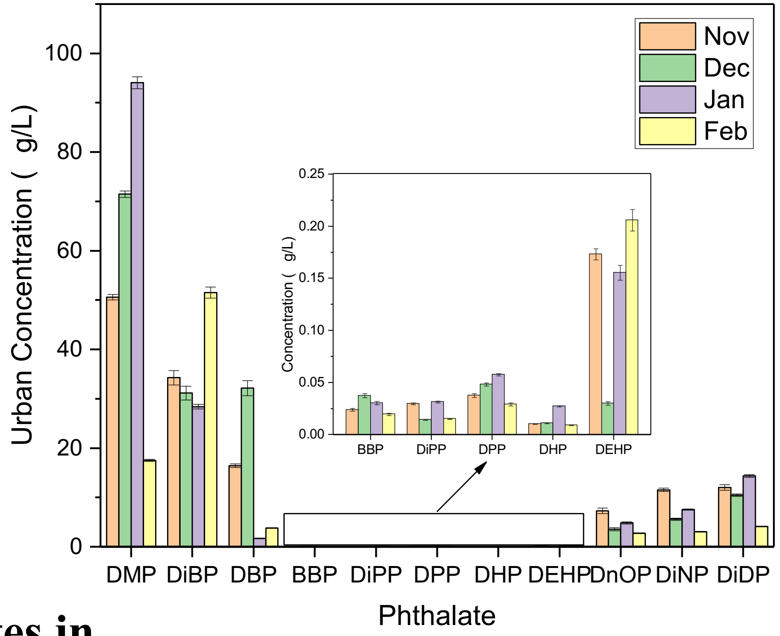


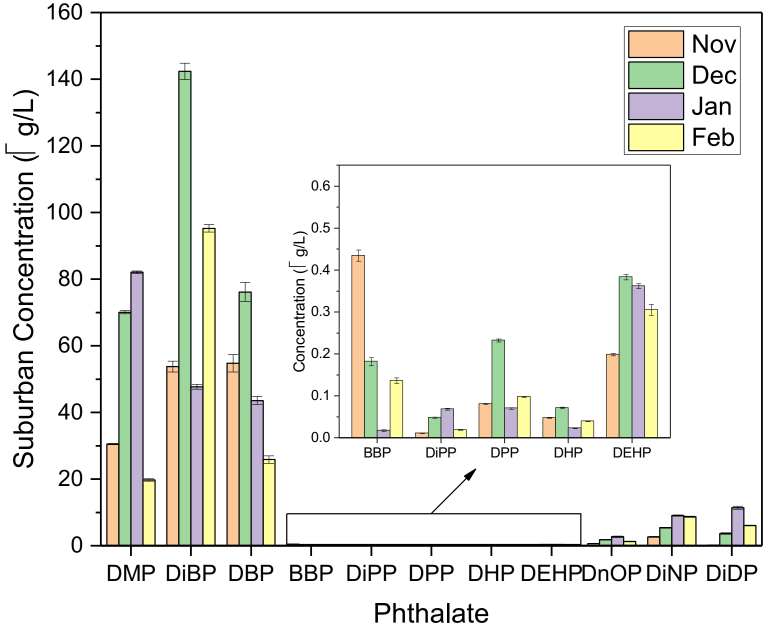


Monoester analytical method application to wastewater influent samples.







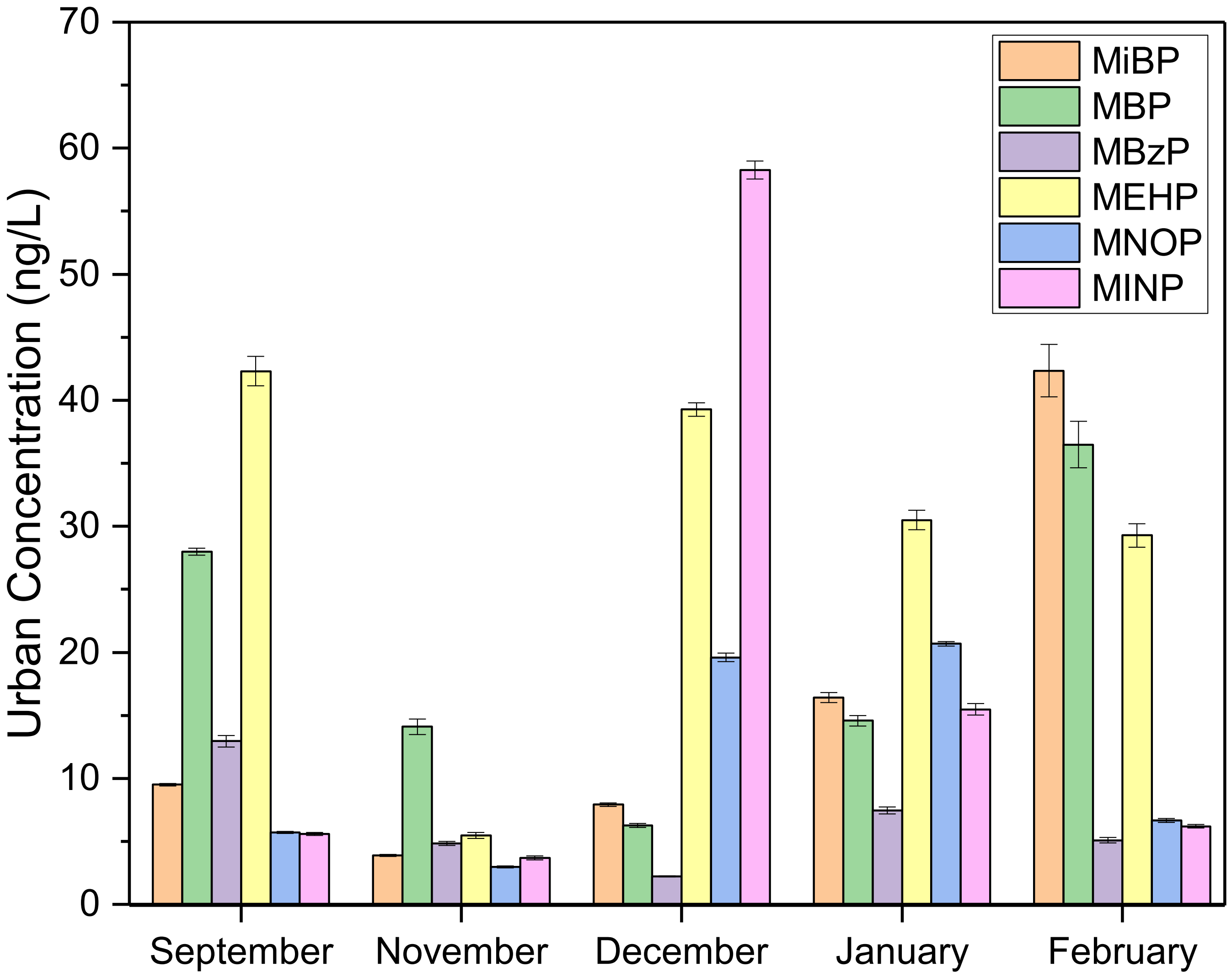


International Comparison of Phthalates in Wastewater Influent (µg/L)

Location	DMP	DBP	BBP	DEHP	DOP	Reference
U.K*	0.26	2.54	1.46	23.6	0.11	(Oliver et al., 2005)
France*	1.5	4.1	4.0	33.3	0.7	(Tran et al., 2015)
Austria	N.D.– 2.4	N.D.– 8.7	0.31– 3.2	3.4– 34.0	N.D.– 1.1	(Clara et al., 2010)
China	4.05– 6.49	8.73– 24.46	N.D.– 5.67	2.42– 30.99	4.63– 12.84	(Gao et al., 2014)
South Africa*	–	0.92– 18.26	N.D.– 6.54	N.D.– 53.21	–	(Gani and Kazmi, 2019)
Ireland	0.80- 95.76	0.58- 78.60	0.01- 0.60	0.03- 0.48	0.08- 7.85	**This Study
India	–	0.928– 18.06	0.90– 19.63	9.17– 218.4	–	(Gani et al., 2016)
South Africa	0.89– 24.51	3.12– 2497	N.D. – 52.25	6.16– 96.18	3.08– 67.37	(Salaudeen et al., 2018)
Puerto Rico*	520	13020	16920	7490	–	(Soler-Llavina et al., 2017)

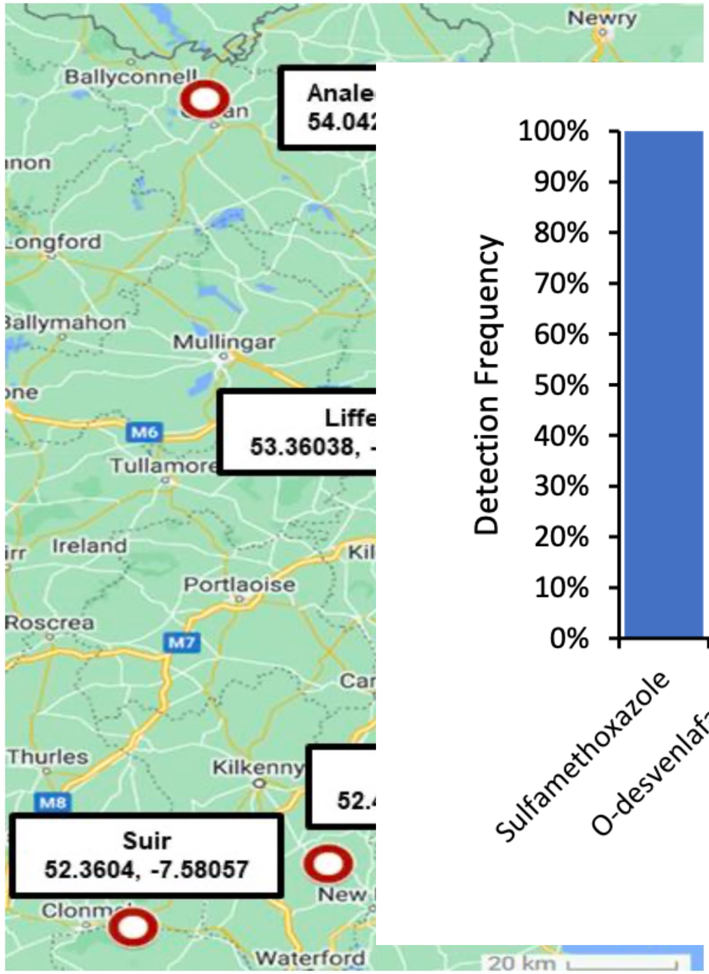
International Comparison of Phthalates in Sludge Reported in mg/kgdw

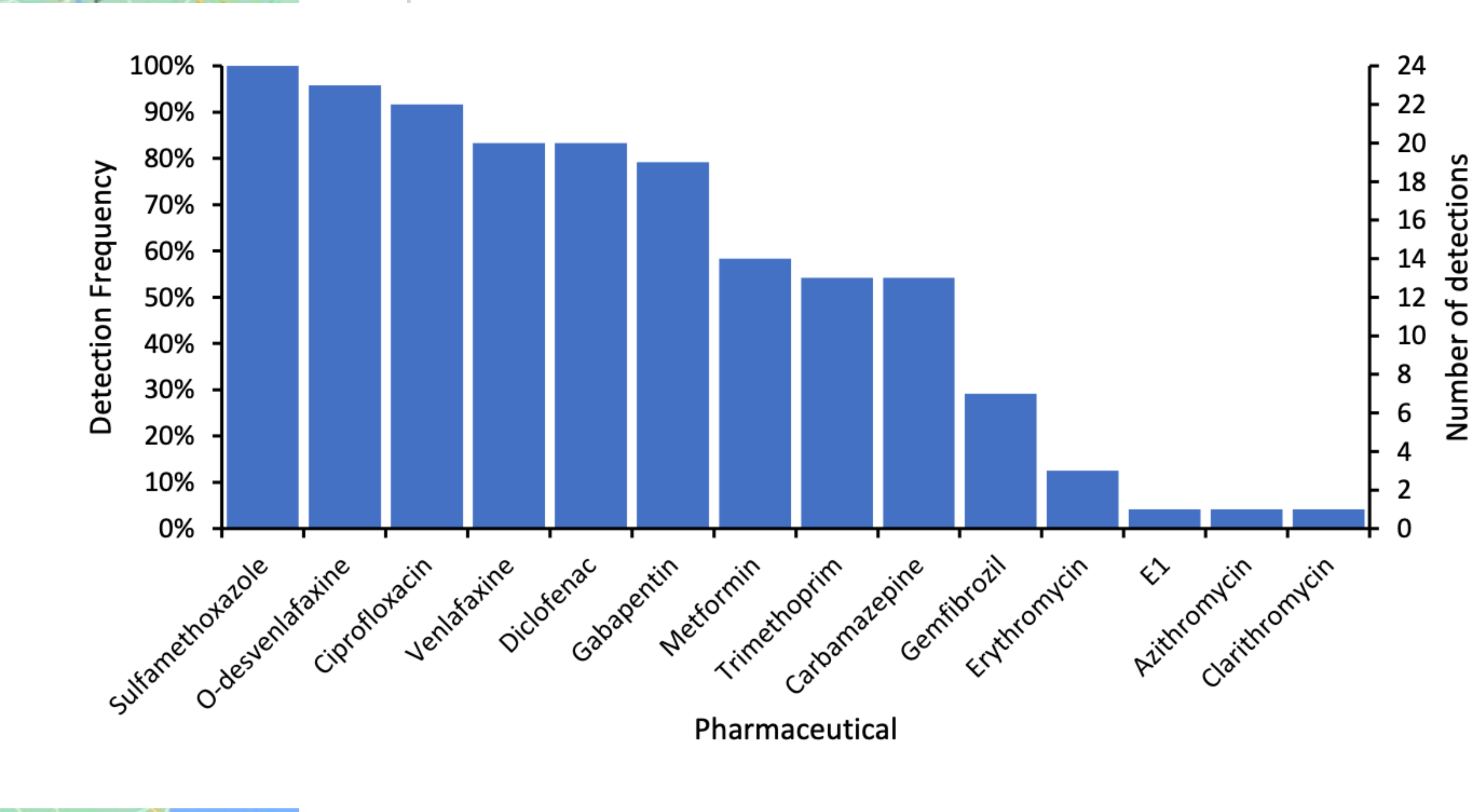
Samples	DMP	DBP	BBP	DEHP	DOP	Reference
China	0.19– 0.91	0.54– 1.94	N.D.– 6.89	1.85– 9.41	1.11– 8.09	(Gao et al., 2014)
U.K.*	0.04	0.97	1.45	30.2	0.14	(Oliver et al., 2005)
France*	2.7	0.09	0.37	72.1	1.9	(Dargnat et al., 2009)
South Africa	–	0.13– 3.16	N.D.– 10.21	N.D.– 76.47	–	(Gani and Kazmi, 2019)
Ireland	6.76- 90.84	24.65- 314.23	1.43- 41.53	6.75- 74.55	0.19-7.46	**This Study
Turkey	1.4-2.7	0.6-4.6	2.8-6.2	18-490	–	(Çifci et al., 2013)
South Africa	6.00-6.10	939- 1248.6	277-621.8	271-352.7	71.9-94.9	(Salaudeen et al., 2018)
Korea	0.0024– 17.00	0.58- 59.00	N.D.-1.90	1.40-1000	–	(Lee et al., 2019)



Urban Concentration (ng/L)
0
10
20
30
40
50
60
70
September
November
December
January
February
MiBP
MBP
MBzP
MEHP
MNOP
MINP

Pharmaceuticals selected, their chemical structures and prioritisation

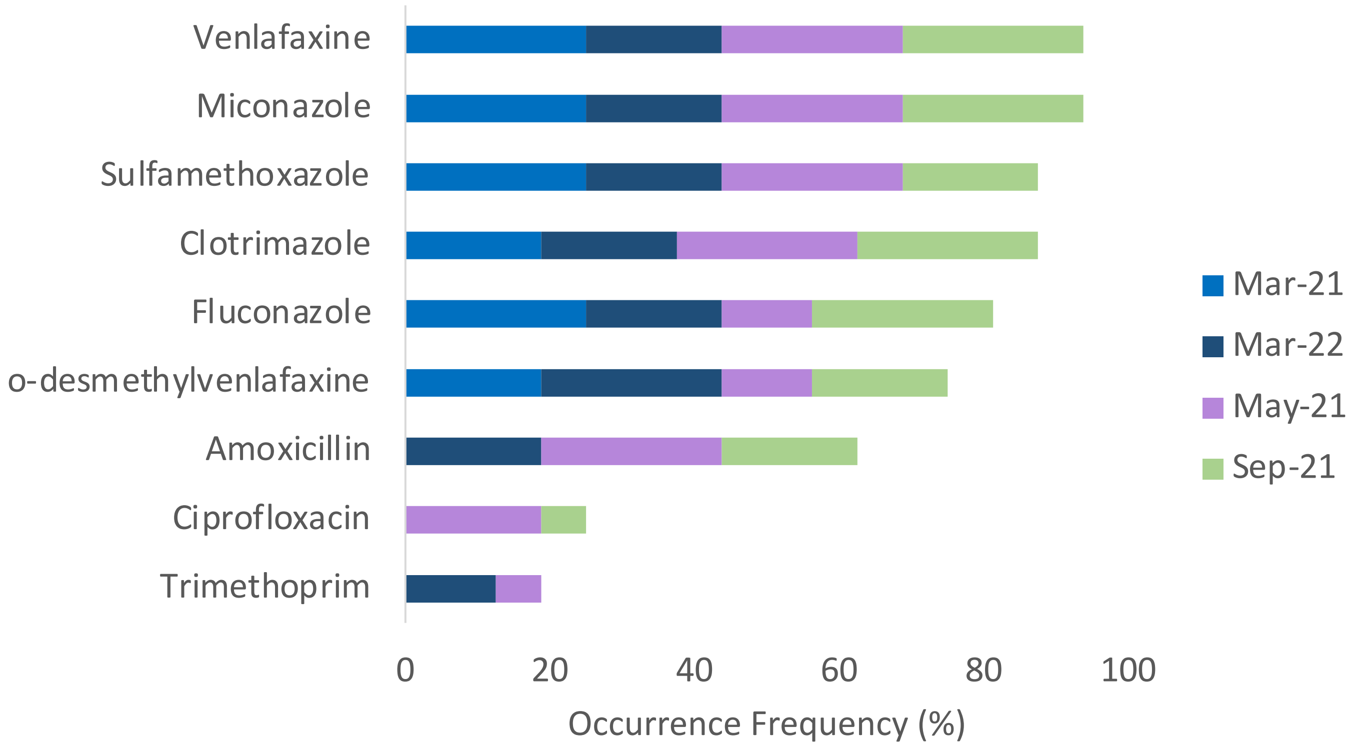


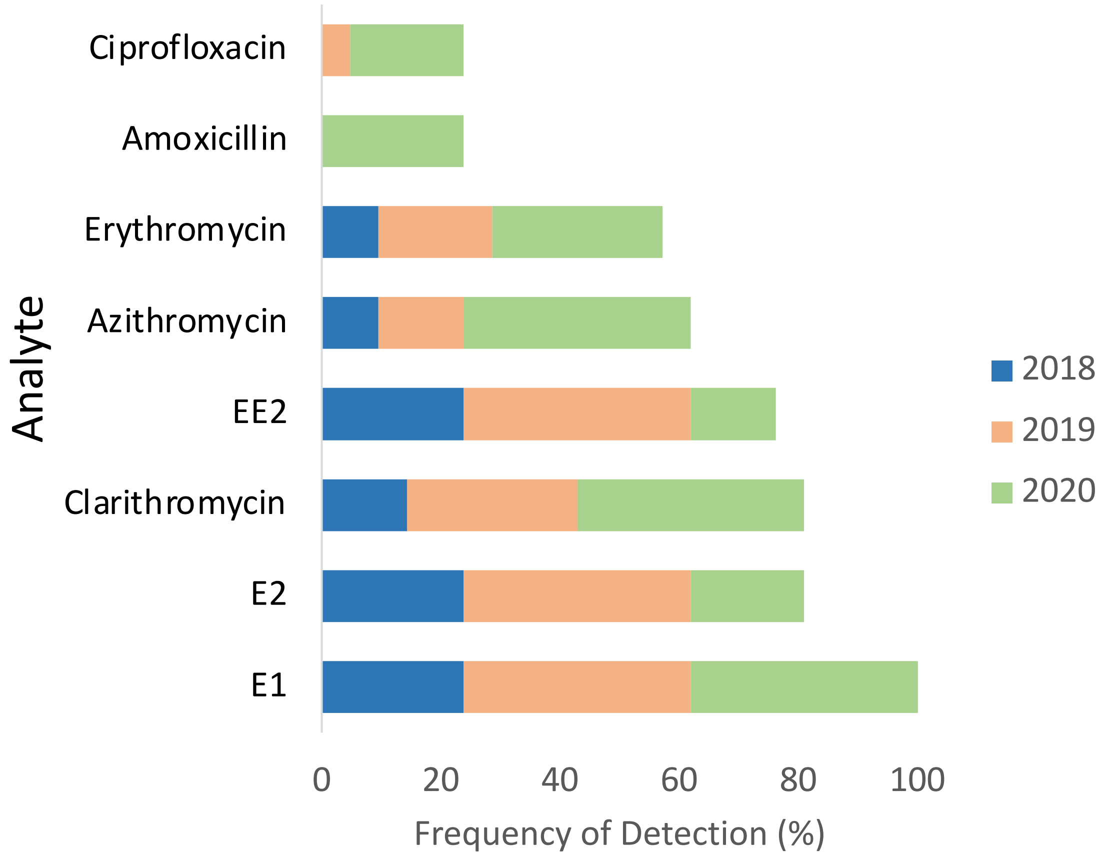


Provisional Candidate for 5th watch list
Priority substance
Priority substance
Priority substance
Priority substance
Priority substance

Pharmaceutical occurrence

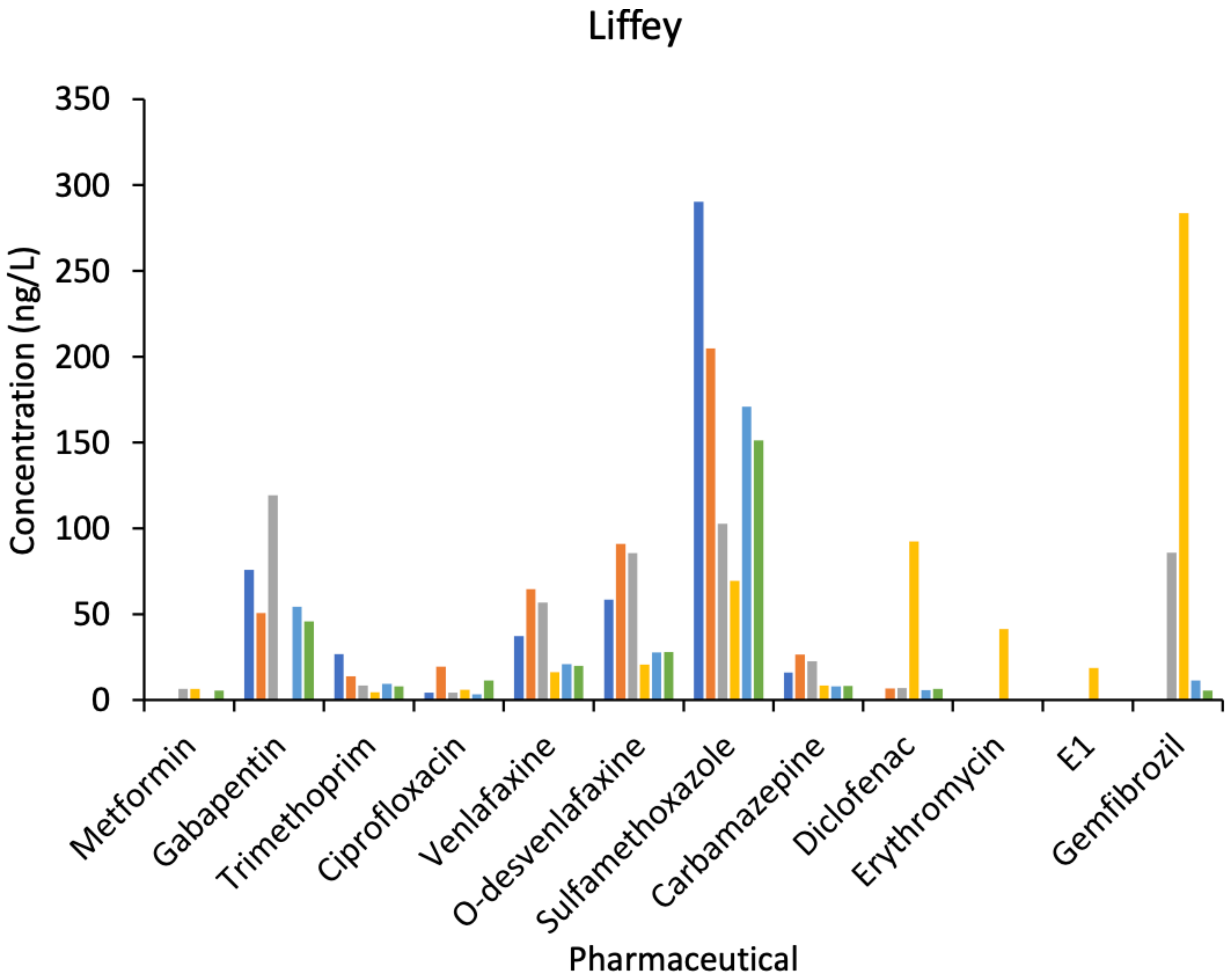
- Watch List Monitoring



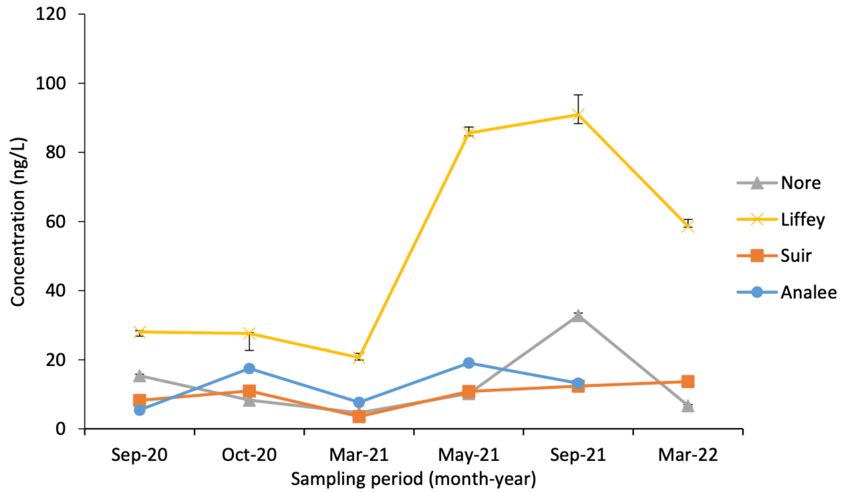


Risk

Analyte	RQ from highest MEC	Risk category	Occurring in sample
Tetraconazole	0.0005 – 0.008	Low	Multiple <LOQ
Penconazole	0.004 - 0.006	Low	Multiple <LOQ
Imazalil	0.002 – 0.003	Low	Multiple <LOQ
Miconazole	0.01 – 0.015	Low	Multiple <LOQ
Tebuconazole	0.071	Low	Liffey September 2021
Fluconazole	0.095	Low	Nore March 2022
Metaflumizone	0.046 – 0.139	Low - *Moderate*	Multiple <LOQ
Ipconazole	0.047 – 0.142	Low - *Moderate*	Multiple <LOQ
Metconazole	0.073 – 0.221	Low- *Moderate*	Multiple <LOQ
Famoxadone	0.121 – 0.368	*Moderate*	Multiple <LOQ
Amoxicillin	0.122	*Moderate*	Nore March 2022
Thiacloprid	0.157 – 0.482	*Moderate*	Multiple <LOQ
Prochloraz	0.168	*Moderate*	Suir September 2021
Dimoxystrobin	0.181	*Moderate*	Liffey March 2022
Sulfamethoxazole	0.200	*Moderate*	Liffey September 2021
Clotrimazole	0.235	*Moderate*	Suir March 2022
Ciprofloxacin	0.281	*Moderate*	Suir May 2021
Trimethoprim	0.320	*Moderate*	Suir May 2021
Clothianidin	0.361	*Moderate*	Liffey December 2018
Azithromycin	0.474	*Moderate*	Liffey December 2018
O-desmethylvenlafaxine	0.500	*Moderate*	Liffey May 2021
Clarithromycin	0.632	*Moderate*	Liffey December 2018
Imidacloprid	0.964	*Moderate*	Liffey August 2019
Erythromycin	1.895	High	Liffey August 2019
Acetamiprid	2.289	High	Suir December 2018
Venlafaxine	2.333	High	Annalee May 2021
Methiocarb	1.015 - 3.05	High	Multiple <LOQ
Thiamethoxam	8.313	High	Suir December 2018
Estrone (E1)	42.7 - 295	High	Multiple <LOQ
Estradiol (E2)	1233.333	High	Annalee August 2019
Ethinylestradiol (EE2)	2166.667	High	Suir August 2019



Liffey
Concentration (ng/L)
350
300
250
200
150
100
50
0
Metformin
Gabapentin
Trimethoprim
Ciprofloxacin
Venlafaxine
O-desvenlafaxine
Sulfamethoxazole
Carbamazepine
Diclofenac
Erythromycin
E1
Gemfibrozil
Pharmaceutical



120
100
80
60
40
20
0
Concentration (ng/L)
Sep-20
Oct-20
Mar-21
May-21
Sep-21
Mar-22
Sampling period (month-year)
Nore
Liffey
Suir
Analee

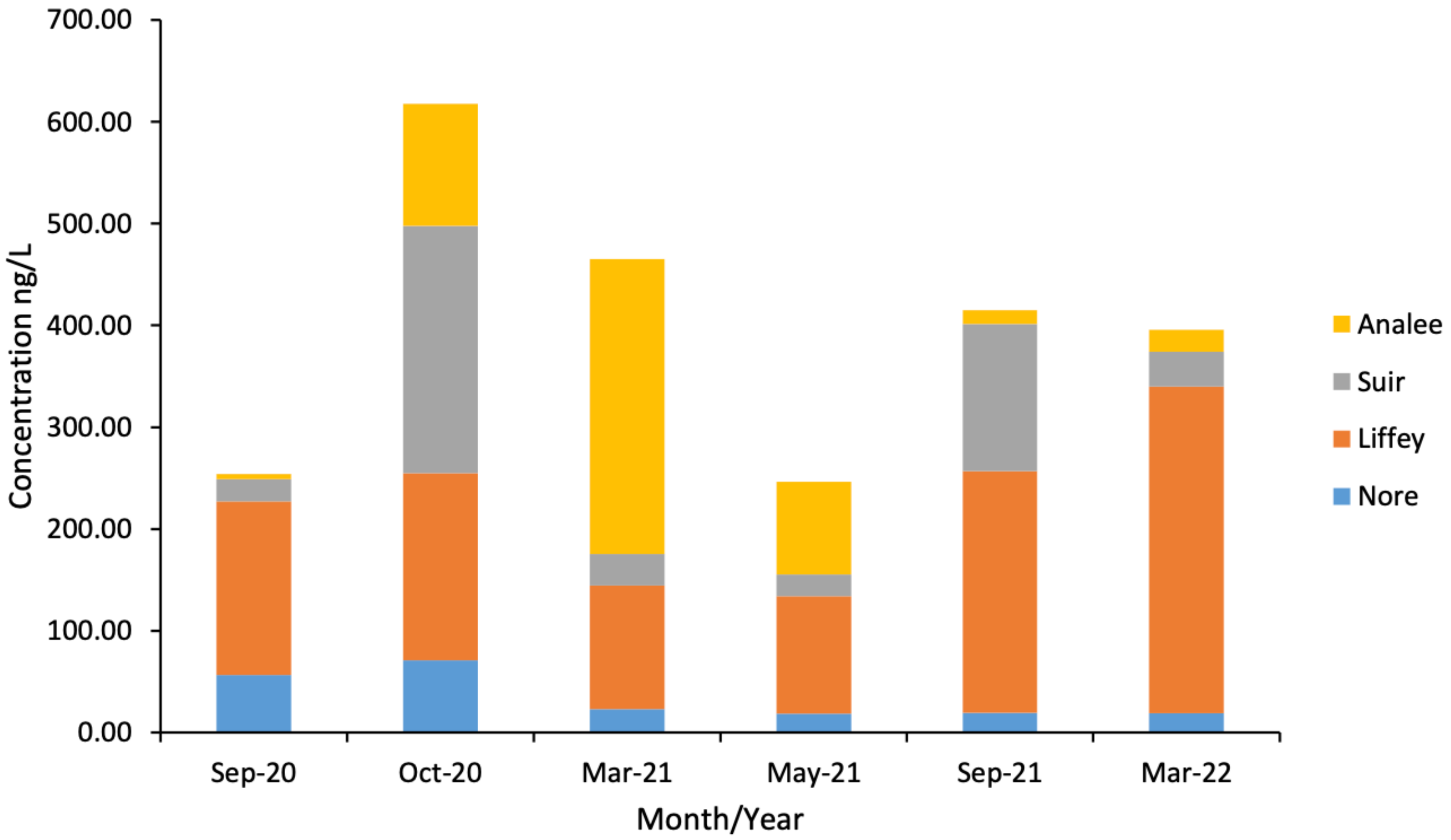
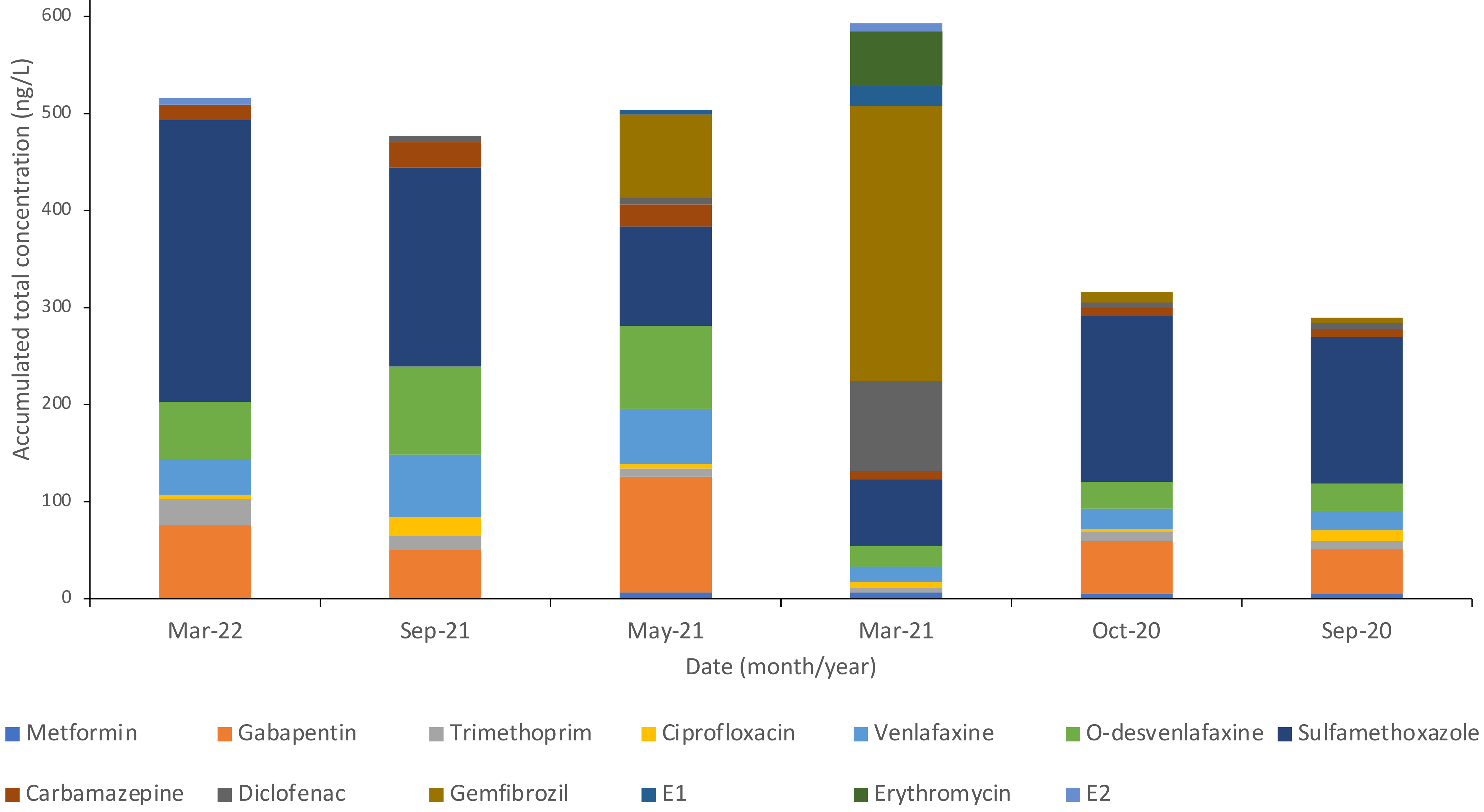


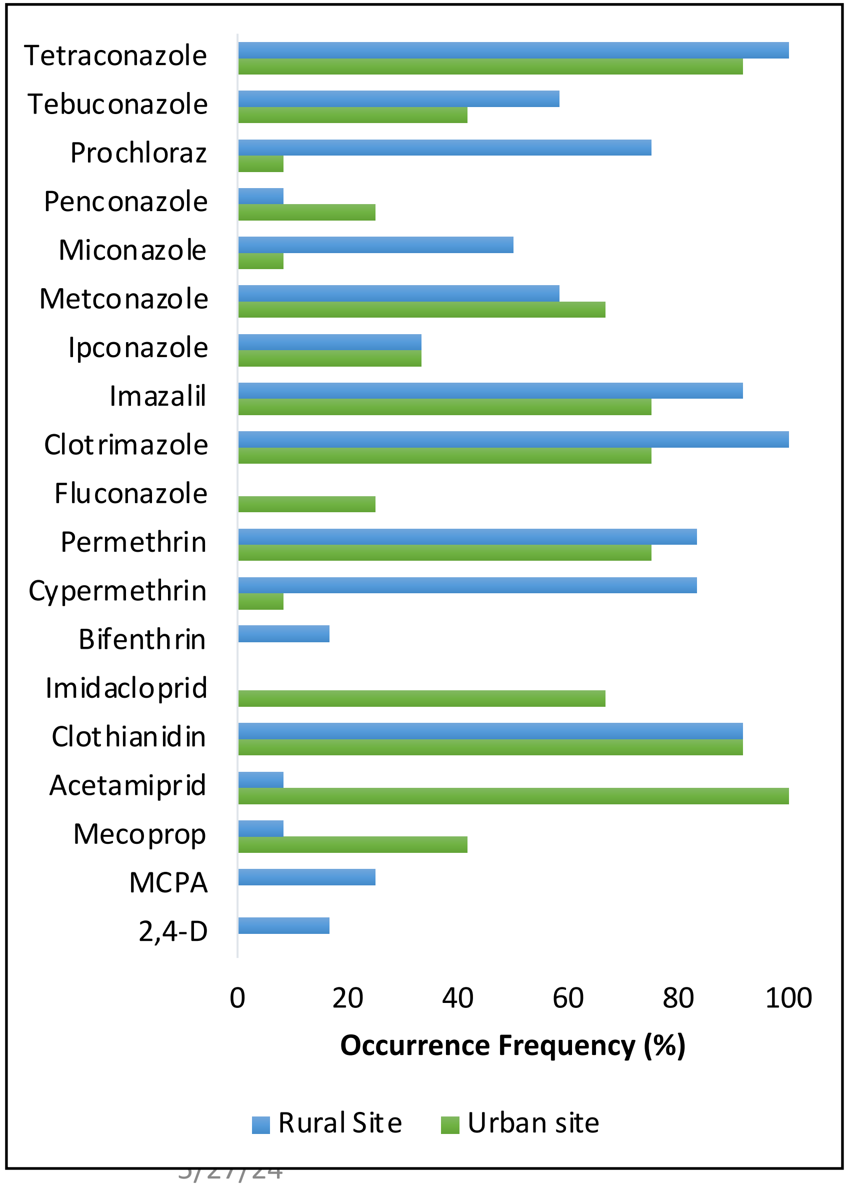
Figure 31: Temporal variation in combined concentration of the antibiotics sulfamethoxazole, ciprofloxacin, trimethoprim, azithromycin, clarithromycin, erythromycin across The Rivers Nore, Liffey, Suir and Analee from 2020 to 2022.



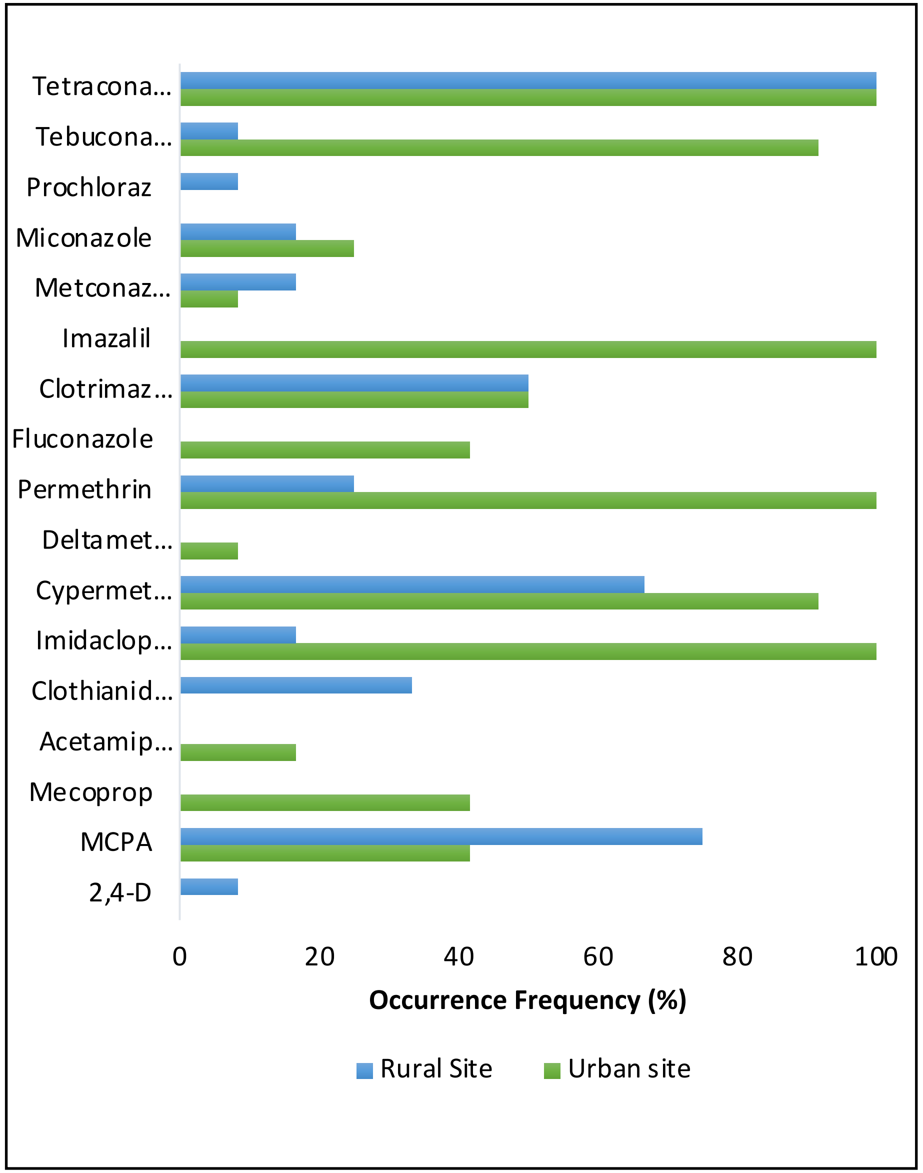
Accumulated total concentration (ng/L)
600
500
400
300
200
100
0
Mar-22
Sep-21
May-21
Mar-21
Oct-20
Sep-20
Date (month/year)
Metformin
Gabapentin
Trimethoprim
Ciprofloxacin
Venlafaxine
O-desvenlafaxine
Sulfamethoxazole
Carbamazepine
Diclofenac
Gemfibrozil
E1
Erythromycin
E2

Pesticide Occurrences

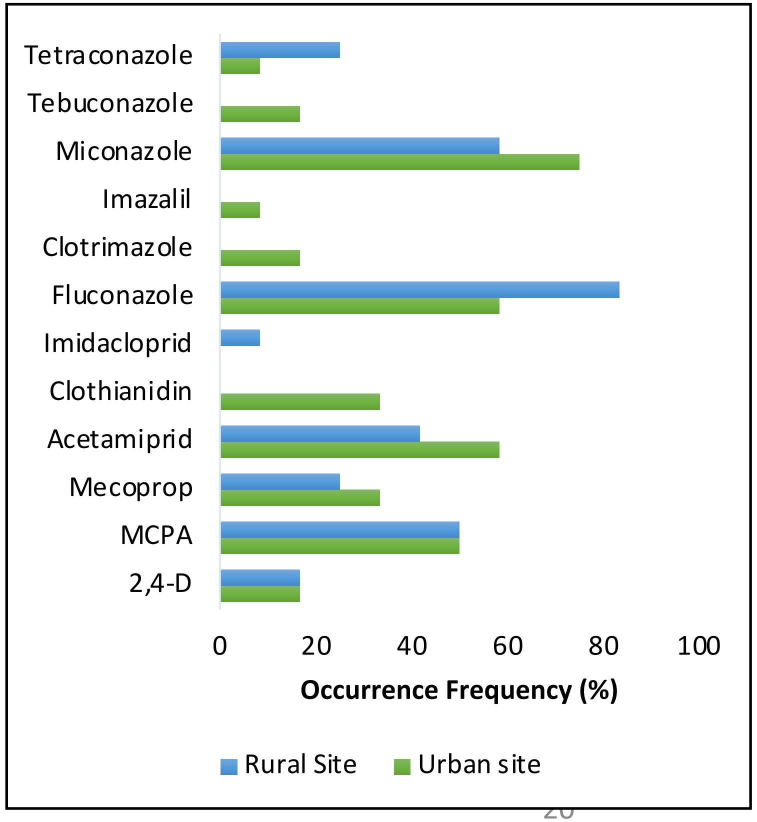
Wastewater Influent

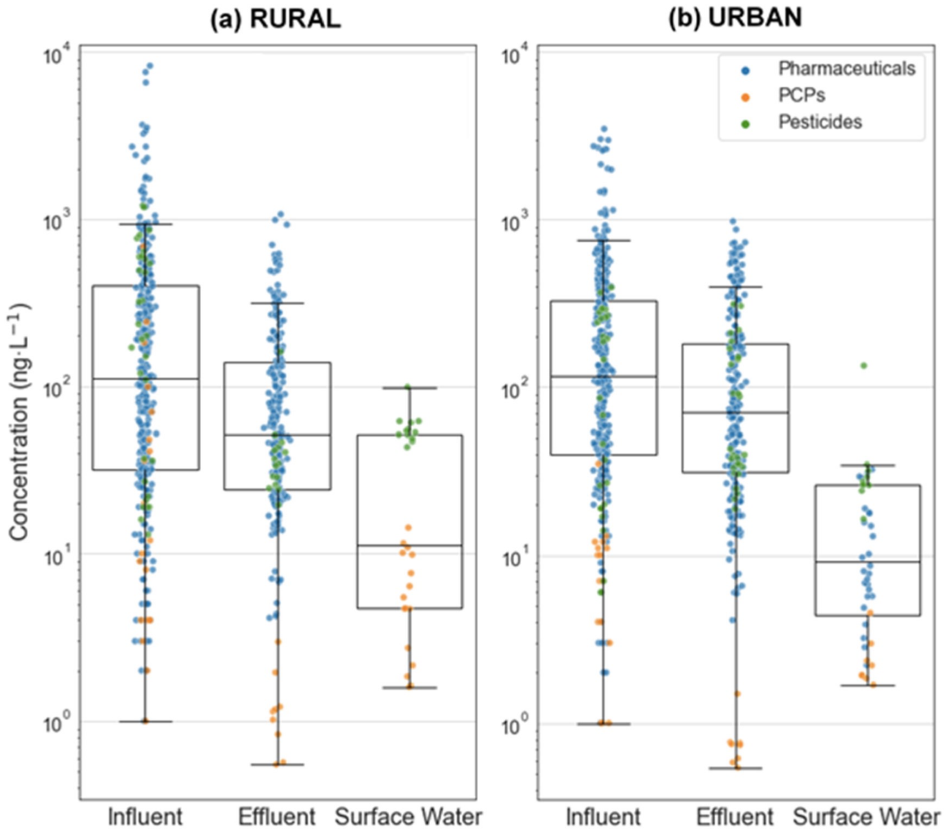


Effluent



Receiving Waters

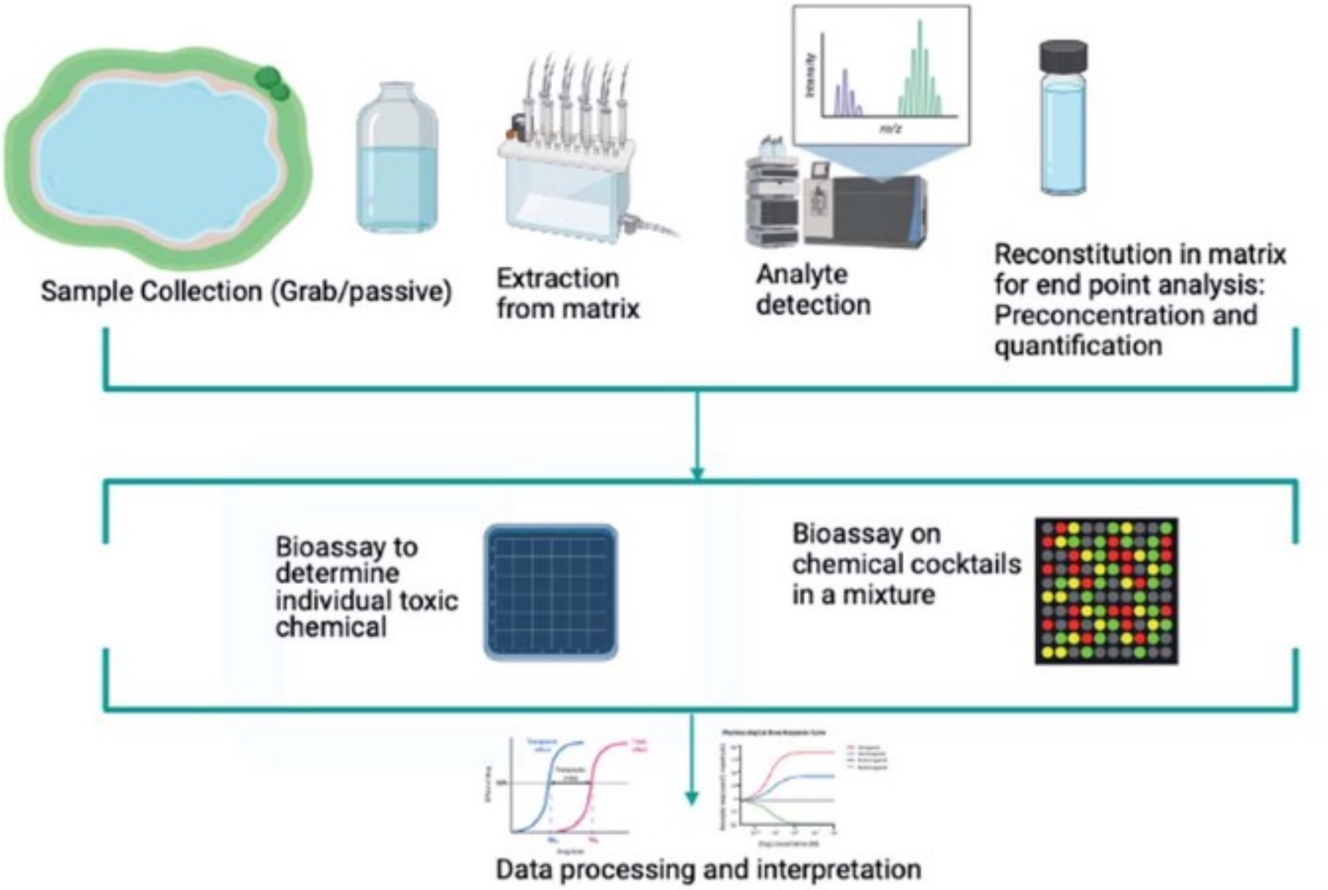




Combined concentrations of all CECs (colour-coded by class) measured in the rural (a) and urban areas (b) across the year-long campaign.

Biological Effects

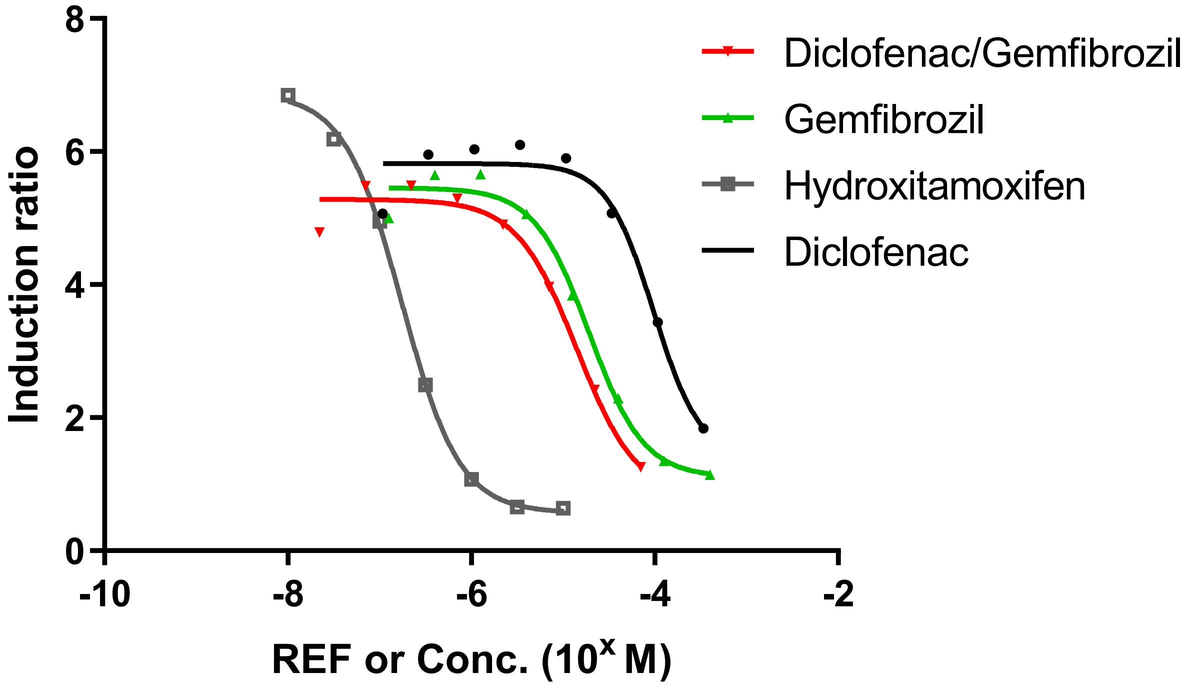
- Anti-estrogenic
- Algal inhibition tests



A typical workflow for assessment of water samples to determine biological effects of chemicals

Cocktail of diclofenac and gemfibrozil shows anti-estrogenic activity at low concentration compared to individual drugs

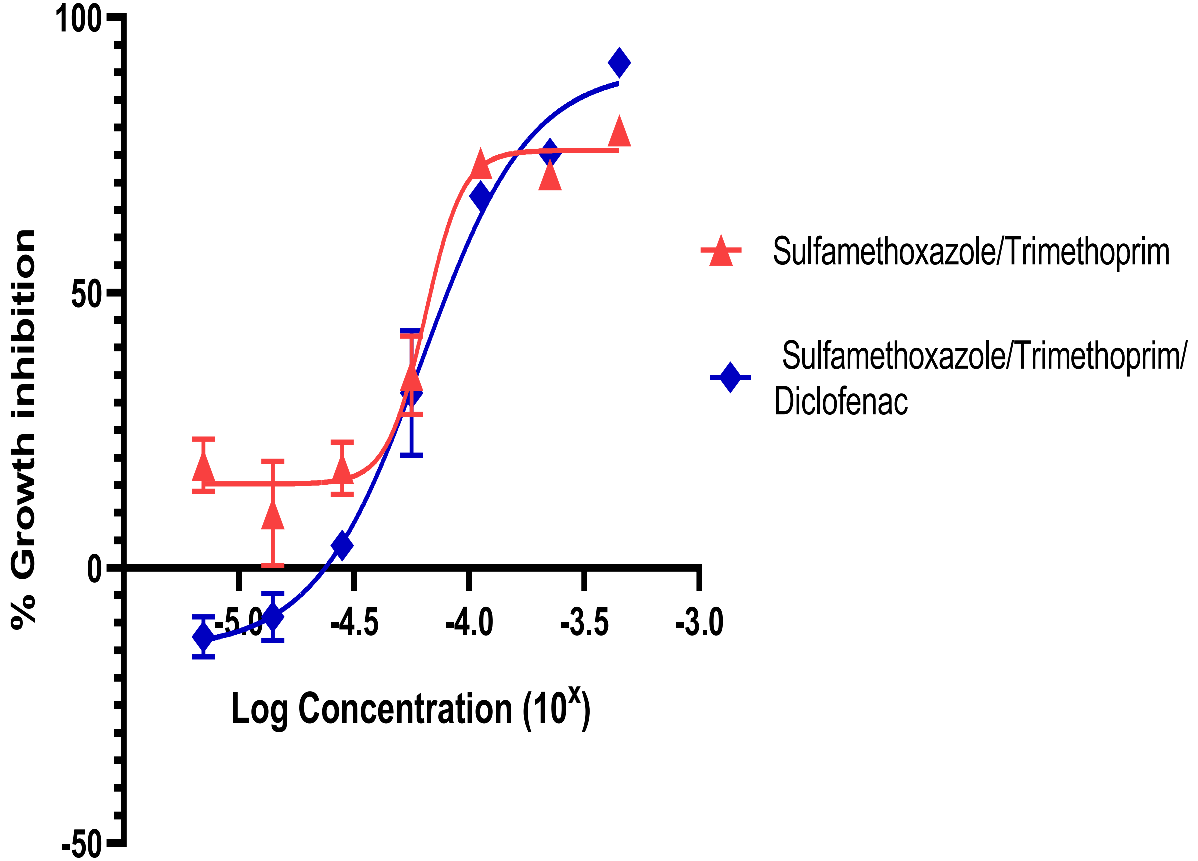
- Mixture of gemfibrozil and diclofenac at 20 mg/L each
- Individual drug at 100 mg/L
- Exposure for 24 h



Cocktail effect of diclofenac and gemfibrozil on antagonising estrogen receptor activities

Mixture effect based on modelled CA

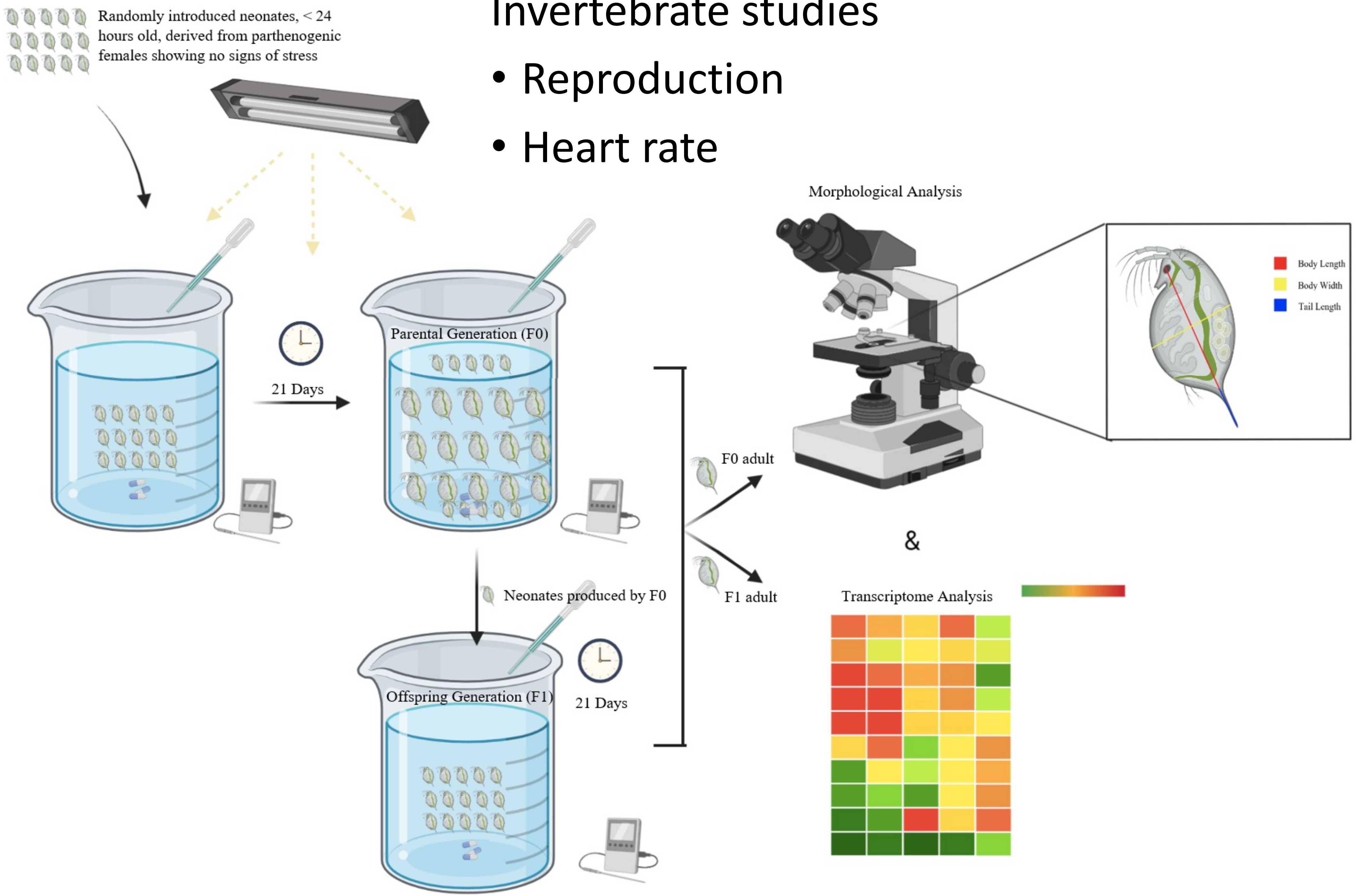
- Exposure concentration from CA prediction (120 h)
- $IC_{mix} = \sum_{k=1}^{n} (\frac{P_k}{IC_{yk}})^{-1}$
- concn range used predicted to have 5% to 95% growth inhibition
- ST achieved 18.66% to 85% and STD achieved -12.67% to 96.8% inhibition

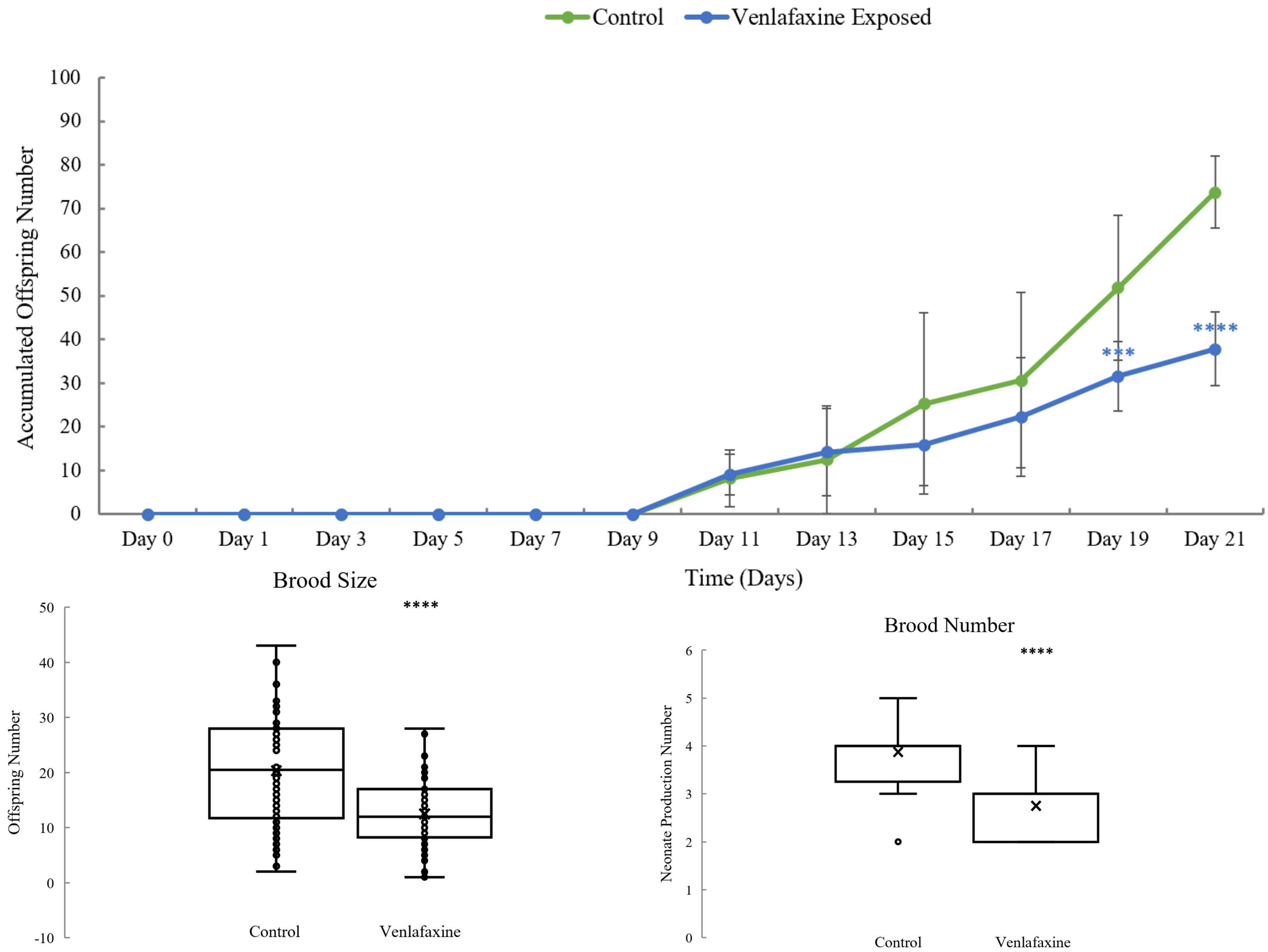


- *Dolichospermum flos aquae*. exposure for 96 h
- Concenrations around the IC50 of sulfamethoxazole used for both S and T
- Diclofenac IC50 selected for S, T and D cocktail

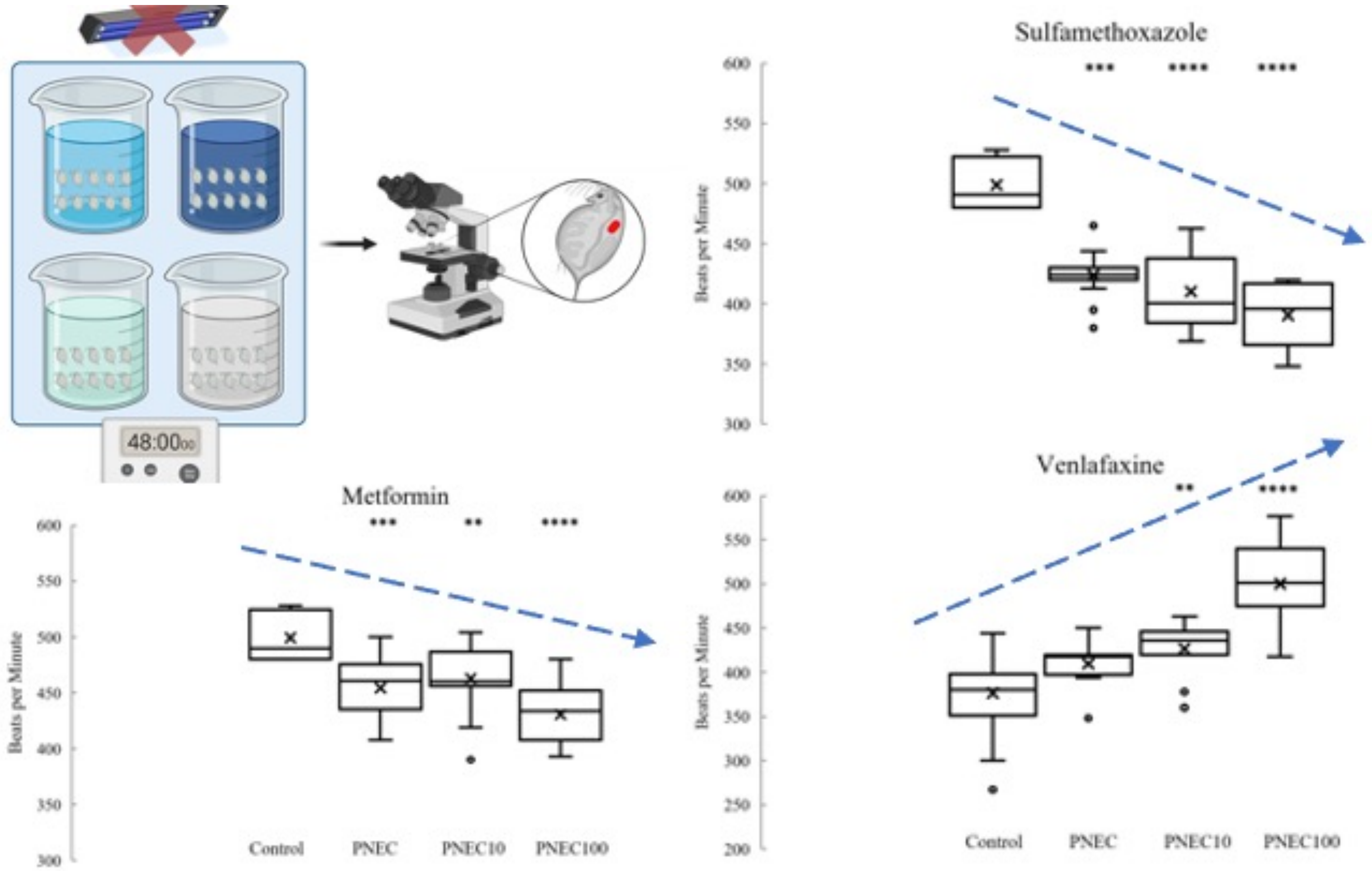
Invertebrate studies

- Reproduction
- Heart rate





Control
Venlafaxine Exposed
Accumulated Offspring Number
100
90
80
70
60
50
40
30
20
10
0
Day 0
Day 1
Day 3
Day 5
Day 7
Day 9
Day 11
Day 13
Day 15
Day 17
Day 19
Day 21
***
****
Time (Days)
Brood Size
Offspring Number
50
40
30
20
10
0
-10
****
Control
Venlafaxine
Brood Number
Neonate Production Number
6
5
4
3
2
1
0
****
Control
Venlafaxine


48:00
Sulfamethoxazole
Metformin
Venlafaxine
Beats per Minute
***
****
**
Control
PNEC
PNEC10
PNEC100
600
550
500
450
400
350
300
250
200

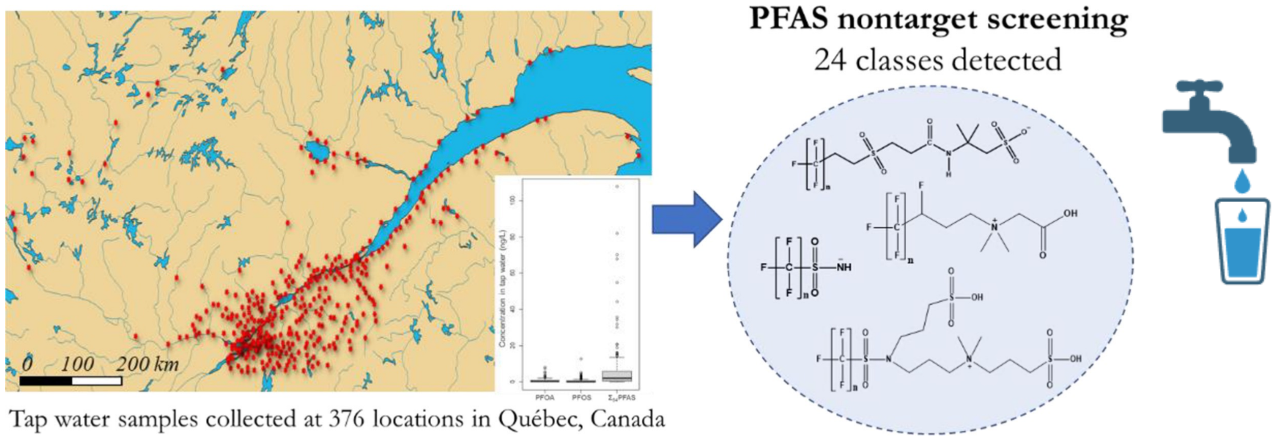
Assessment of the Occurrence and Distribution of Per- and Polyfluoroalkyl Substances in the River Liffey

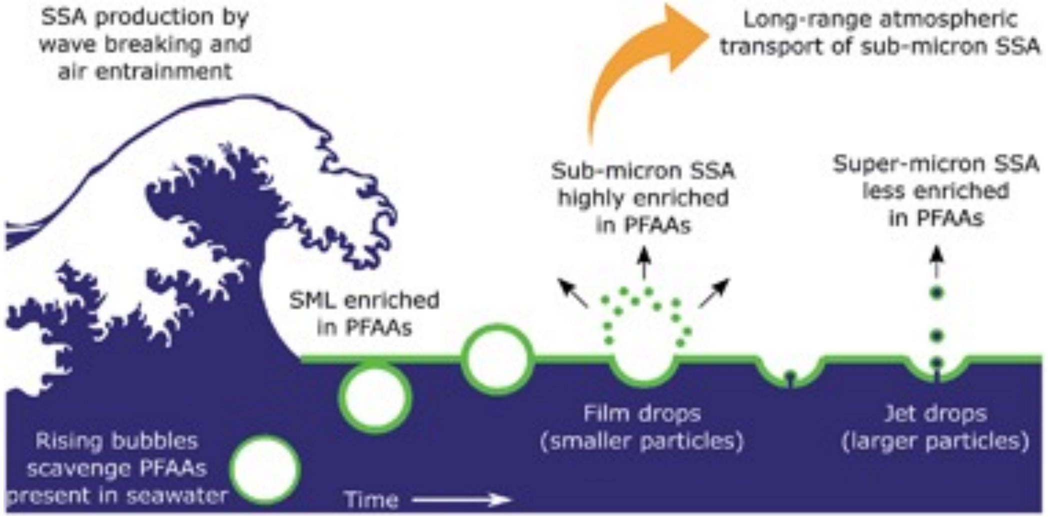
DCU Institiúid Uisce DCU DCU Water Institute

INVEST pFASST

- Ubiquitous in the environment

Health concerns





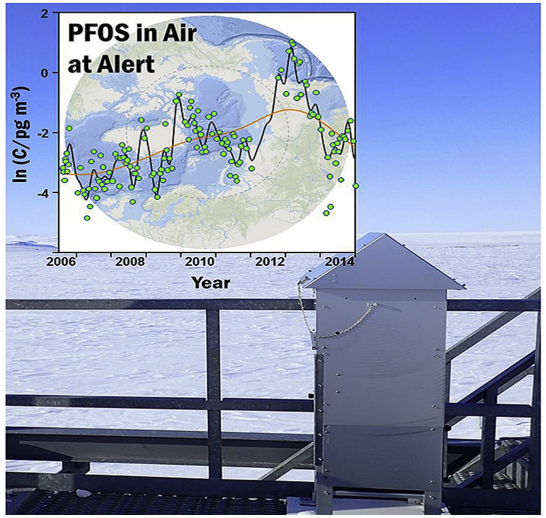
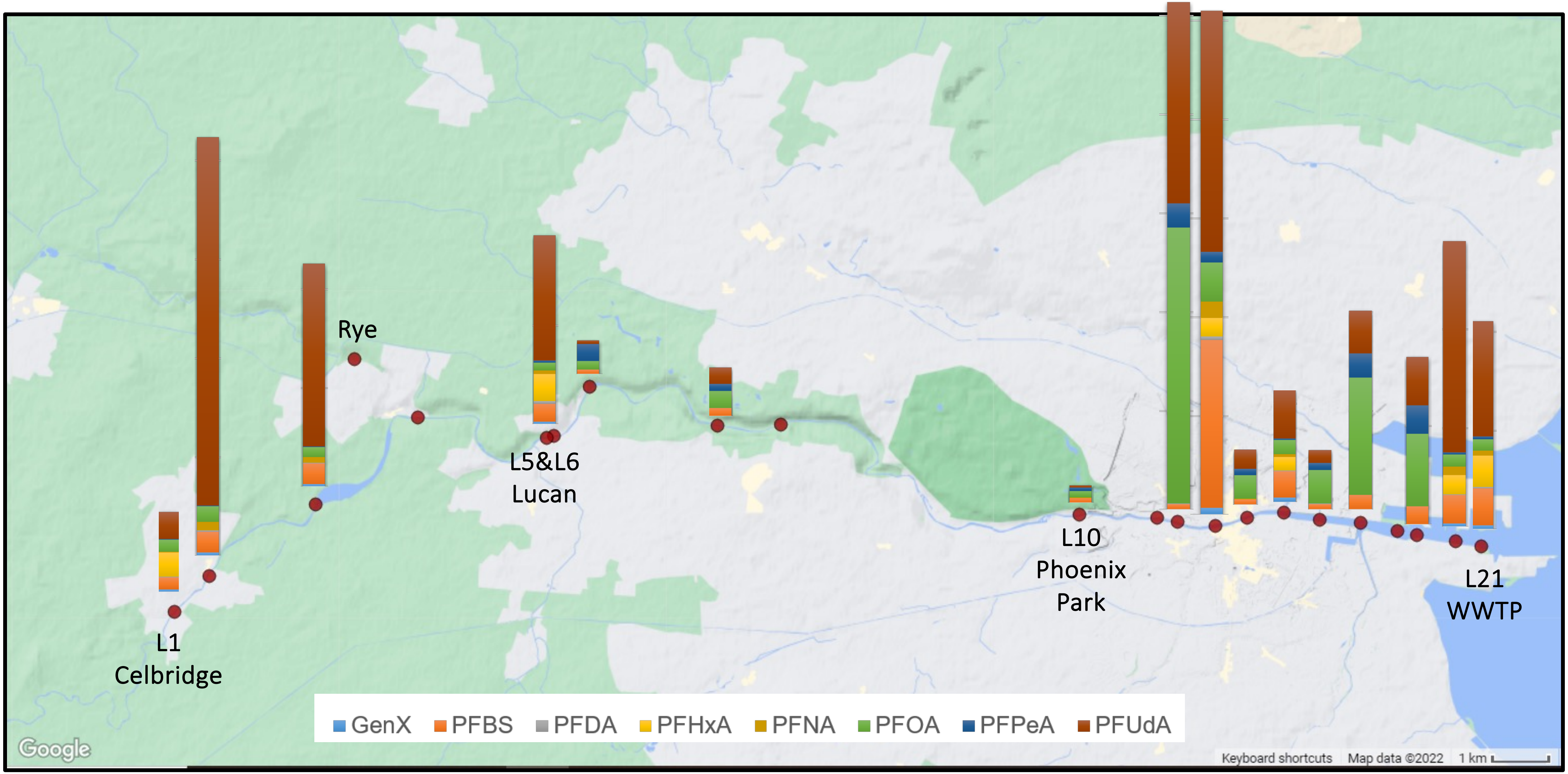


Table 1 Description of target analytes included in the present study

Compound	Acronym	CAS number	Class	Fluorinated C chain	Formula
Perfluorododecanoate	PFDoA	307-55-1	Acid	C12	$C_{12}HF_{23}O_2$
Perfluoroundecanoate	PFUdA	2058-94-8	Acid	C11	$C_{11}HF_{21}O_2$
Perfluorodecanoate	PFDA	335-76-2	Acid	C10	$C_{10}HF_{19}O_2$
Perfluorononanoate	PFNA	375-95-1	Acid	C9	$C_9HF_{17}O_2$
Perfluorooctanoate	PFOA	335-67-1	Acid	C8	$C_8HF_{15}O_2$
Perfluorohexanoate	PFHxA	307-24-4	Acid	C6	$C_6HF_{11}O_2$
Perfluoropropoxypropanoic acid	Gen X	13252-13-6	Acid	C6	$C_6HF_{11}O_3$
Perfluoropentanoate	PFPeA	2706-90-3	Acid	C5	$C_5HF_9O_2$
Perfluorooctanesulfonamide	FOSA	754-91-6	FOSA	C8	$C_8H_2F_{17}NO_2S$
Perfluorodecylsulfonate	PFDS	2806-15-7	Sulfonate	C10	$C_{10}HF_{21}O_3S$
Perfluorononylsulfonate	PFNS	98789-57-2	Sulfonate	C9	$C_9HF_{19}O_3S$
Perfluorooctylsulfonate	PFOS	4021-47-0	Sulfonate	C8	$C_8HF_{17}O_3S$
Perfluorohexylsulfonate	PFHxS	82382-12-5	Sulfonate	C6	$C_6HF_{13}O_3S$
Perfluoropentylsulfonate	PFPeS	630402-22-1	Sulfonate	C5	$C_7HF_{13}O_2$
Perfluorobutylsulfonate	PFBS	29420-49-3	Sulfonate	C4	$C_4HF_9O_3S$
Perfluoro-1-($^{13}C_8$) octanesulfonate	M8PFOS	—	Sulfonate	C8	$^{13}C_8F_{17}SO_3$
Perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$] nonanoic acid	MPFNA	—	Acid	C9	$^{13}C_5{}^{12}C_4HF17O_2$
Perfluoro-*n*-[1,2-$^{13}C_2$] octanoic acid	MPFOA	—	Acid	C8	$^{13}C_2{}^{12}C_6HF_{15}O_2$
Perfluoro-*n*-[1,2-$^{13}C_2$] hexanoic acid	MPFHxA	—	Acid	C6	$^{13}C_2{}^{12}C_4HF_{11}O_2$

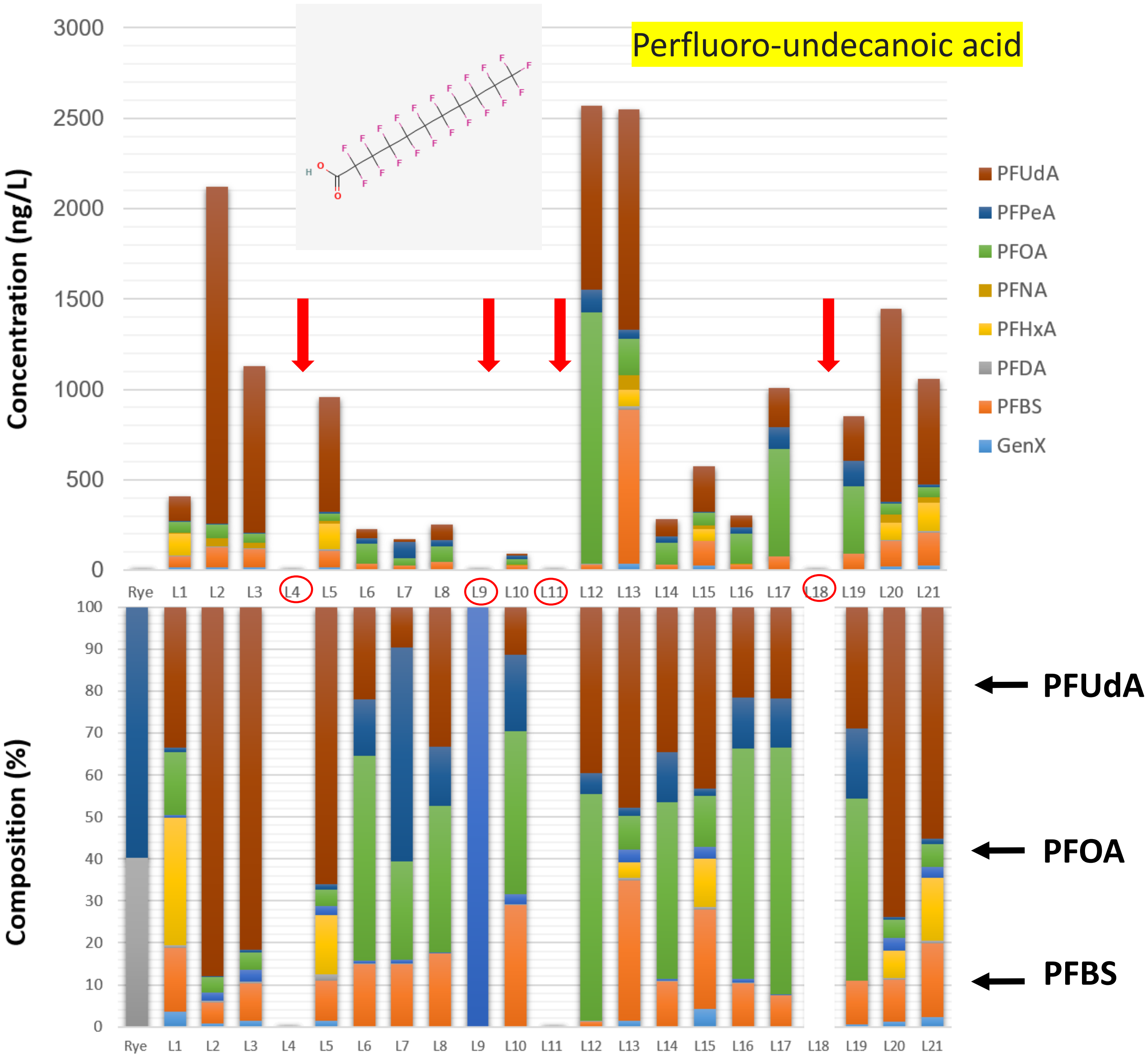
Results: Occurrence



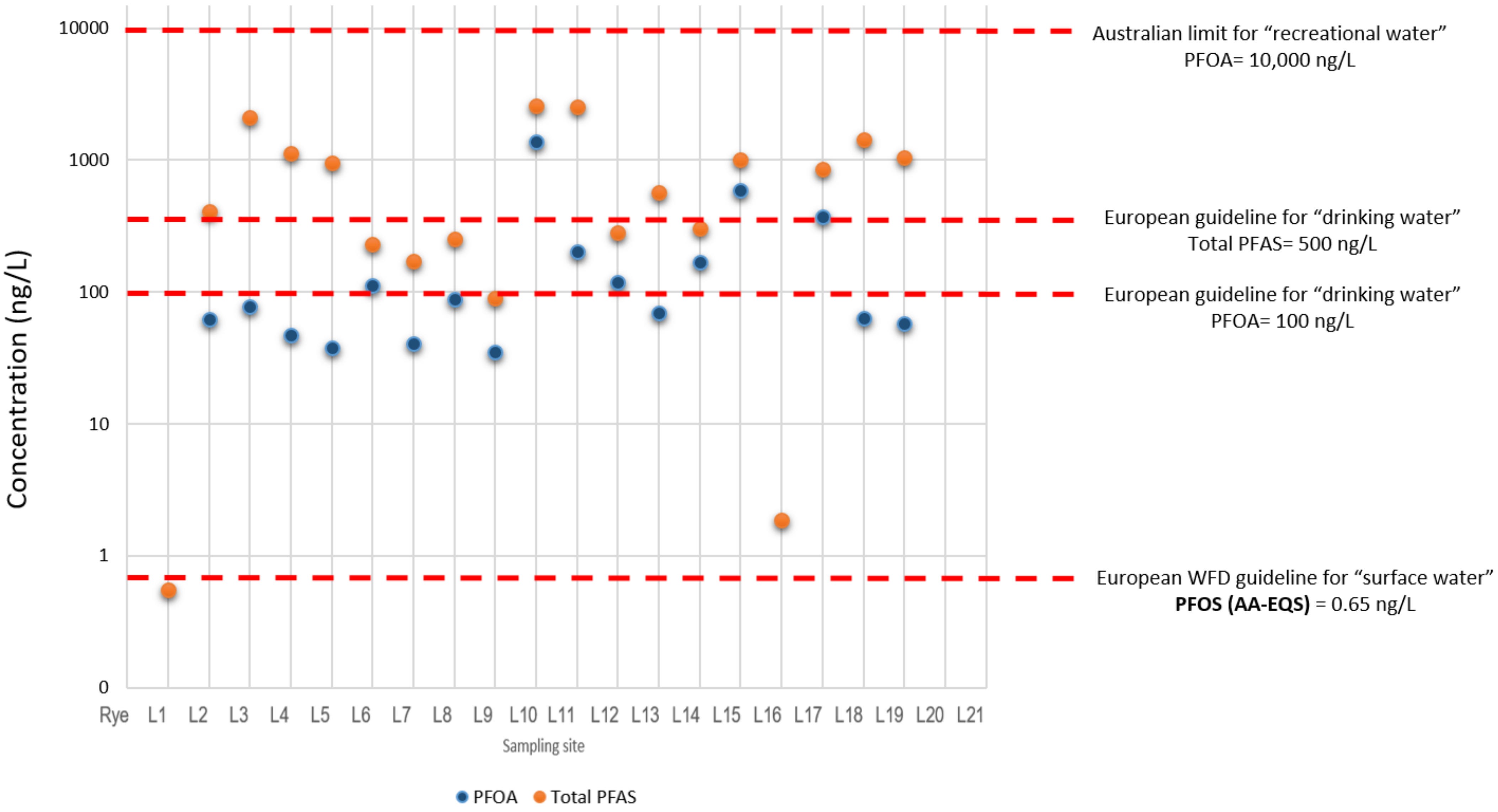
Results: Occurrence

- 8 compounds out of 15 were consistently detected
- PFOS, FOSA, PFDoA, PFDS, PFHxS, PFNS and PFPeS were not detected
- 4 samples had no PFAS → potential extraction issue

- Concentrations in the low ng/L to µg/L
  Highest concentrations were detected for the compound **PFUdA** (up to 1.8 µg/L)
- **PFOA** was detected almost in every sample, with a maximum of 1.2 µg/L
- **PFBS** was detected consistently in almost all samples(up to 0.8 µg/L)



Guidelines


10000
1000
100
10
1
0
Concentration (ng/L)
Rye
L1
L2
L3
L4
L5
L6
L7
L8
L9
L10
L11
L12
L13
L14
L15
L16
L17
L18
L19
L20
L21
Sampling site
PFOA
Total PFAS
Australian limit for "recreational water" PFOA= 10,000 ng/L
European guideline for "drinking water" Total PFAS= 500 ng/L
European guideline for "drinking water" PFOA= 100 ng/L
European WFD guideline for "surface water" PFOS (AA-EQS) = 0.65 ng/L

Source Tracking

Apply multivariate analysis for source tracking: PCA and hierarchical clustering to group sites with statistically distinct PFAS composition

Data we need....

- Chemical composition → Continue to sample at locations where there are inputs we can identify;
- Plausible sources
- Hydrological distance from the source to the sampling site → Calculate the hydrological distance – ArcGIS
- Classify points as urban (>1000 inhabitants/km^2) or rural → Find a source of information to determine population for the sub-catchments included in the study

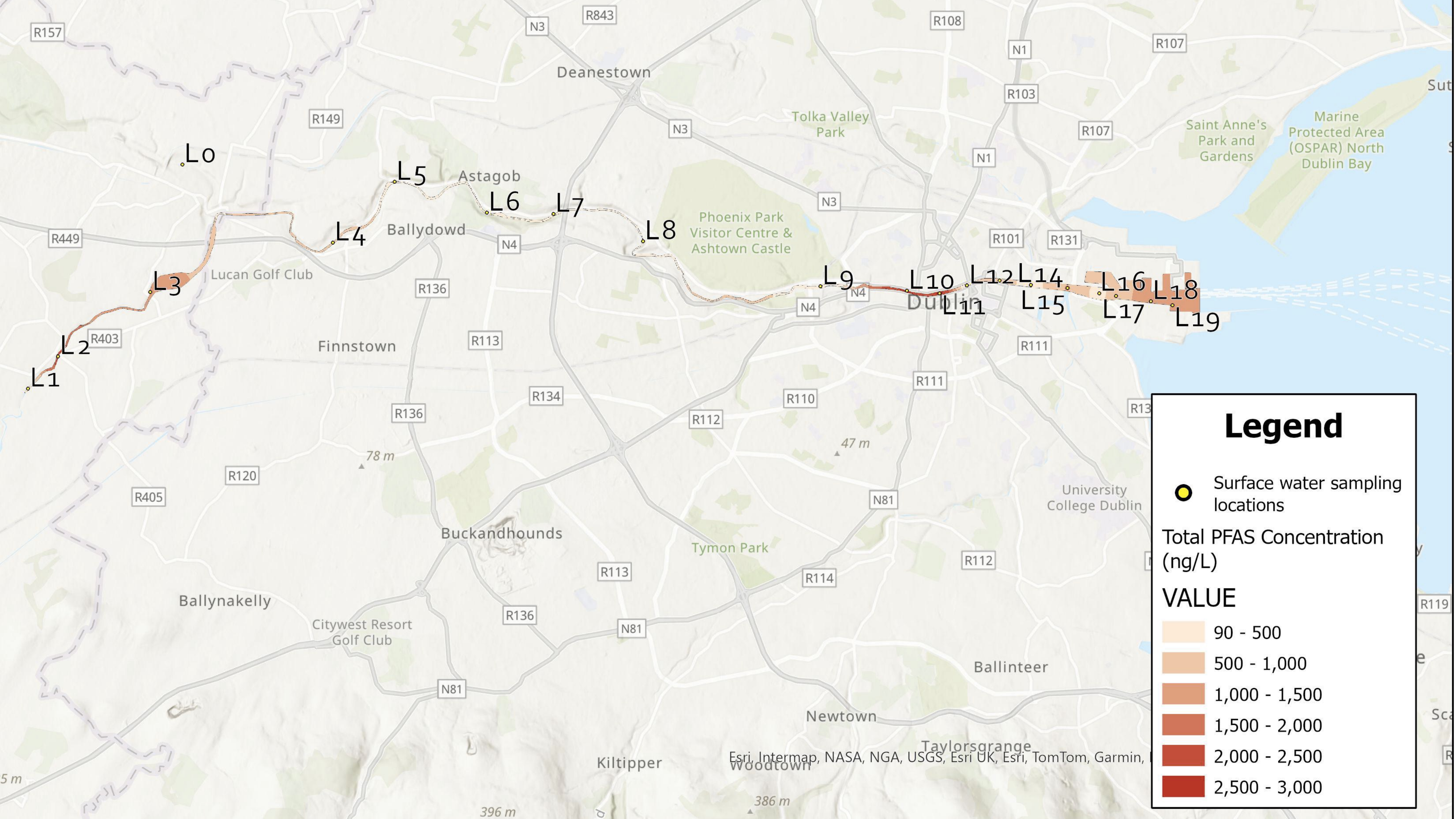
Problems we have....

Continue to sample at locations where there are inputs we can identify;

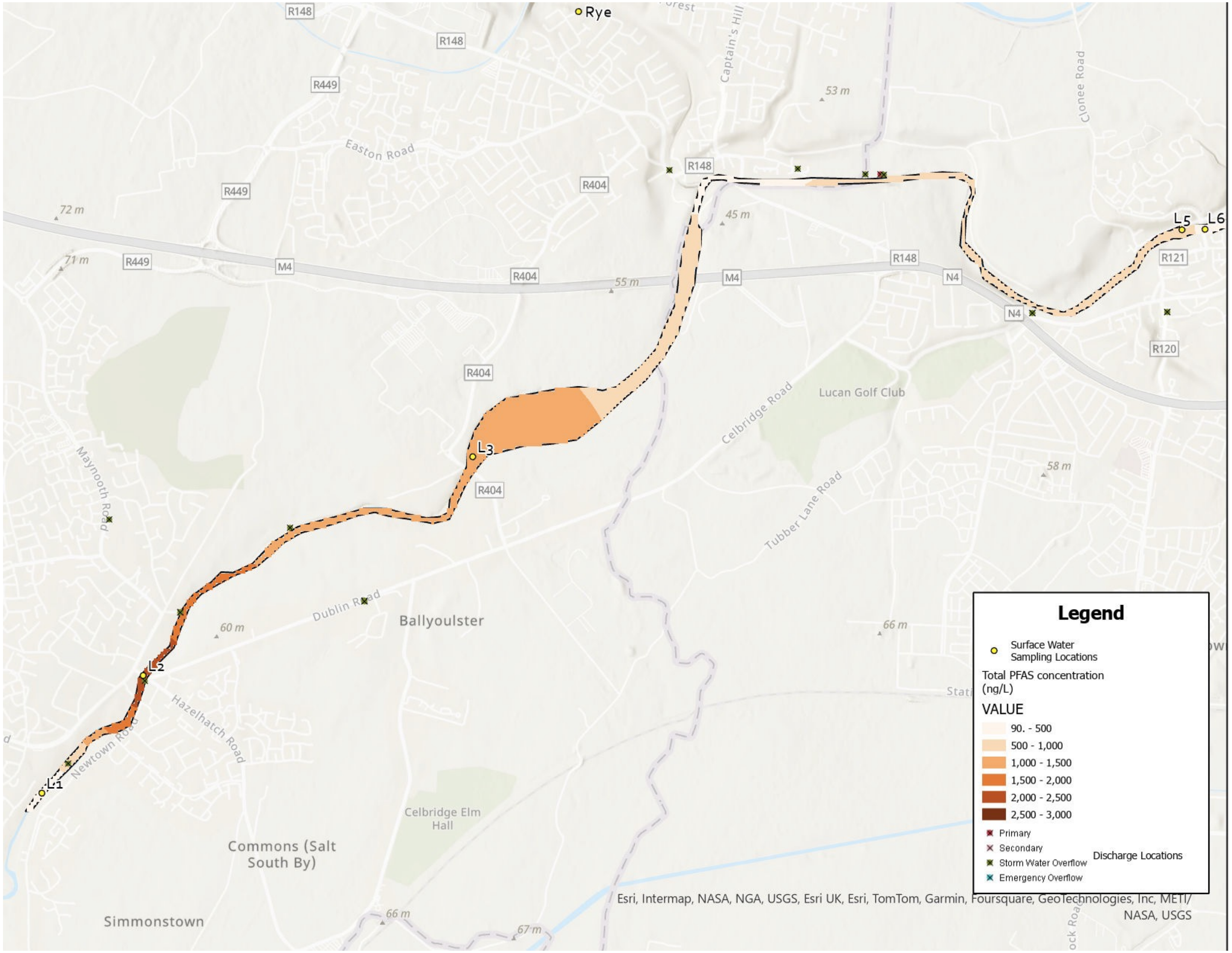
Calculate the hydrological distance – ArcGIS

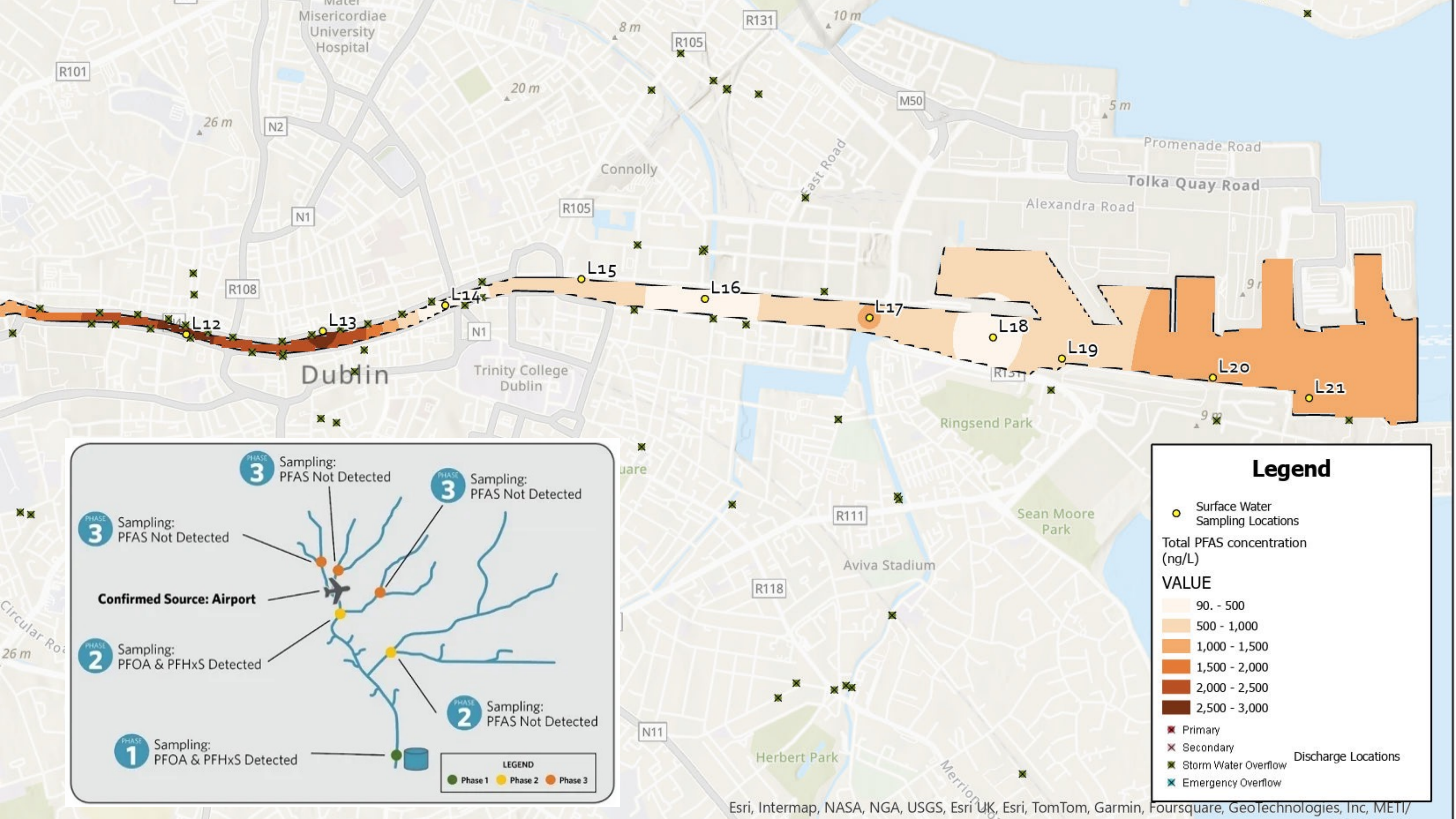
Find a source of information to determine population for the sub-catchments included in the study

➡ Use multivariate analysis properly (variable selection, data normalization, etc.)



L0
L1
L2
L3
L4
L5
L6
L7
L8
L9
L10
L11
L12
L14
L15
L16
L17
L18
L19
Legend
Surface water sampling locations
Total PFAS Concentration (ng/L)
VALUE
90 - 500
500 - 1,000
1,000 - 1,500
1,500 - 2,000
2,000 - 2,500
2,500 - 3,000
Deanestown
Astagob
Ballydowd
Lucan Golf Club
Finnstown
Phoenix Park Visitor Centre & Ashtown Castle
Tolka Valley Park
Saint Anne's Park and Gardens
Marine Protected Area (OSPAR) North Dublin Bay
Dublin
University College Dublin
Tymon Park
Buckandhounds
Ballynakelly
Citywest Resort Golf Club
Ballinteer
Newtown
Taylorsgrange
Kiltipper
Woodtown
Esri, Intermap, NASA, NGA, USGS, Esri UK, Esri, TomTom, Garmin,


Rye
R148
R449
R404
Easton Road
Captain's Hill
Clonee Road
53 m
72 m
71 m
45 m
55 m
M4
R121
R148
N4
R120
L5
L6
L3
L2
L1
Lucan Golf Club
Celbridge Road
Tubber Lane Road
58 m
Maynooth Road
Dublin Road
Ballyoulster
60 m
66 m
Hazelhatch Road
Newtown Road
Celbridge Elm Hall
Commons (Salt South By)
Simmonstown
66 m
67 m
Legend
Surface Water Sampling Locations
Total PFAS concentration (ng/L)
VALUE
90. - 500
500 - 1,000
1,000 - 1,500
1,500 - 2,000
2,000 - 2,500
2,500 - 3,000
Primary
Secondary
Storm Water Overflow
Emergency Overflow
Discharge Locations
Esri, Intermap, NASA, NGA, USGS, Esri UK, Esri, TomTom, Garmin, Foursquare, GeoTechnologies, Inc, METI/NASA, USGS


Mater Misericordiae University Hospital
R101
R105
R131
8 m
10 m
20 m
26 m
N2
M50
5 m
Promenade Road
Tolka Quay Road
Alexandra Road
Connolly
East Road
N1
R105
R108
L12
L13
L14
L15
L16
L17
L18
L19
L20
L21
N1
Dublin
Trinity College Dublin
Ringsend Park
9 m
Sean Moore Park
R111
Aviva Stadium
R118
N11
Herbert Park
Circular Road
26 m
PHASE 3 Sampling: PFAS Not Detected
PHASE 3 Sampling: PFAS Not Detected
PHASE 3 Sampling: PFAS Not Detected
Confirmed Source: Airport
PHASE 2 Sampling: PFOA & PFHxS Detected
PHASE 2 Sampling: PFAS Not Detected
PHASE 1 Sampling: PFOA & PFHxS Detected
LEGEND
Phase 1
Phase 2
Phase 3
Legend
Surface Water Sampling Locations
Total PFAS concentration (ng/L)
VALUE
90. - 500
500 - 1,000
1,000 - 1,500
1,500 - 2,000
2,000 - 2,500
2,500 - 3,000
Primary
Secondary
Storm Water Overflow
Emergency Overflow
Discharge Locations
Esri, Intermap, NASA, NGA, USGS, Esri UK, Esri, TomTom, Garmin, Foursquare, GeoTechnologies, Inc, METI/

Acknowledgements

- Brendan McHugh
- Belinda Huerta
- Helen Burke
- Leila Bowe
- Christopher Newton Arup
- Enrique Diaz-Montana, Chloe Richards
- Marcus Chadha Agilent
- Jonathan Spencer Agilent

I-SECURE

Irish marine screening and assessment of emerging contaminants in coastal and transitional Environments (I-SECURE)

This research (Grant-Aid Agreement No. PDOC/19/03/02) is carried out with the support of the Marine Institute, funded under the Marine Research Programme by the Irish Government.

INVEST pFASST

An INVESTigation of PFAS from Source to sink - to assess risk and inform a PFAS STrategy in Ireland

Foras na Mara Marine Institute

epa Research