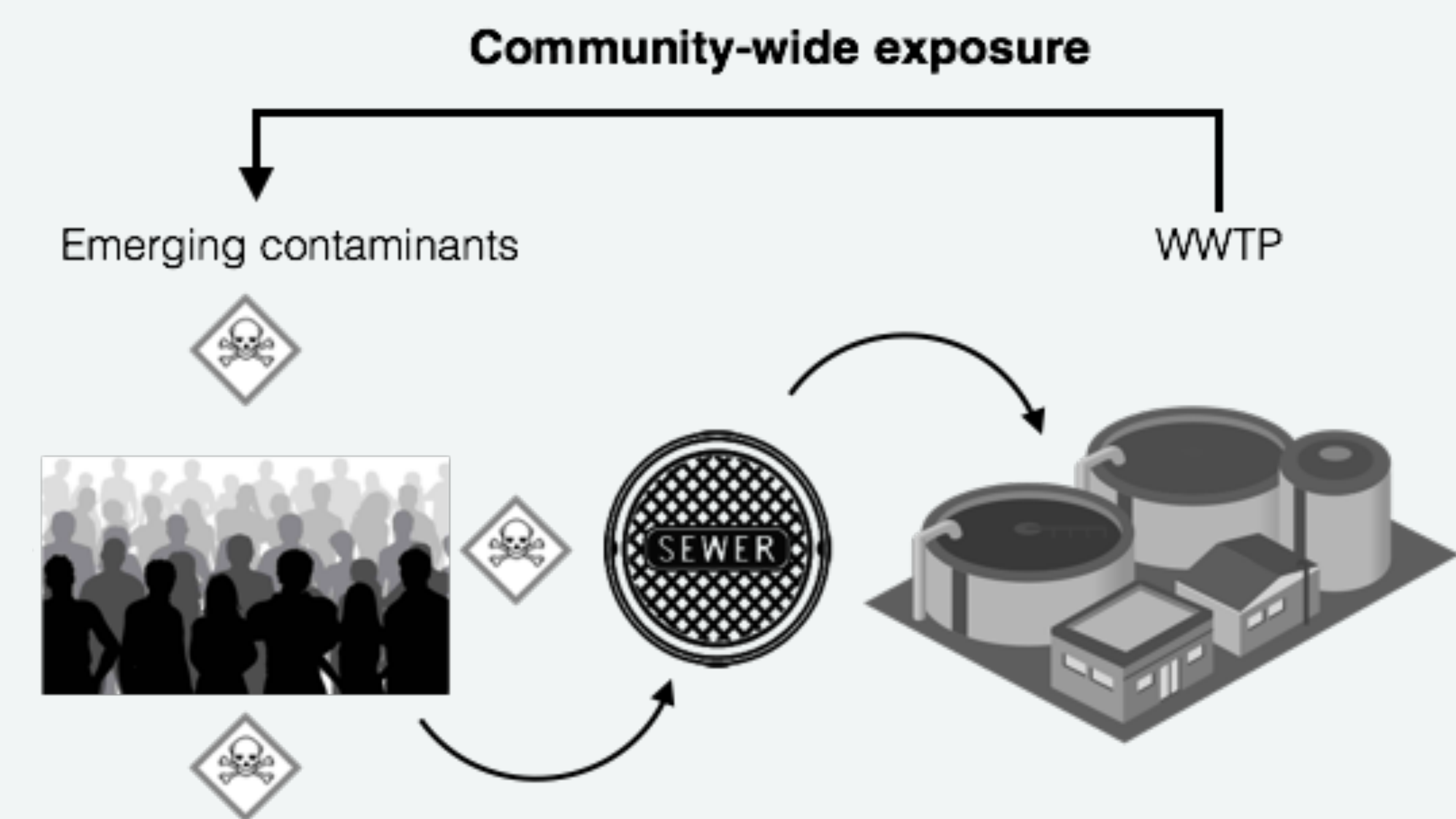


Upscaling human biomonitoring – Wastewater-based epidemiology to assess exposure to organophosphate flame retardants (PFRs)

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Introduction

Phosphorus flame retardants and plasticizers (PFRs) are used as **flame retardants** and **plasticizers** in a wide range of products such as furniture, textile, electronics, PVC, resins and paints. PFRs are not chemically bound to these materials and are therefore easily released and detected in the environment¹. PFRs **may pose a risk** to **human health**: some are suspected carcinogens, neurotoxins and endocrine disruptors. Complementary to classical human biomonitoring², PFR metabolites can be measured in wastewater to assess exposure in the general population.



Aims

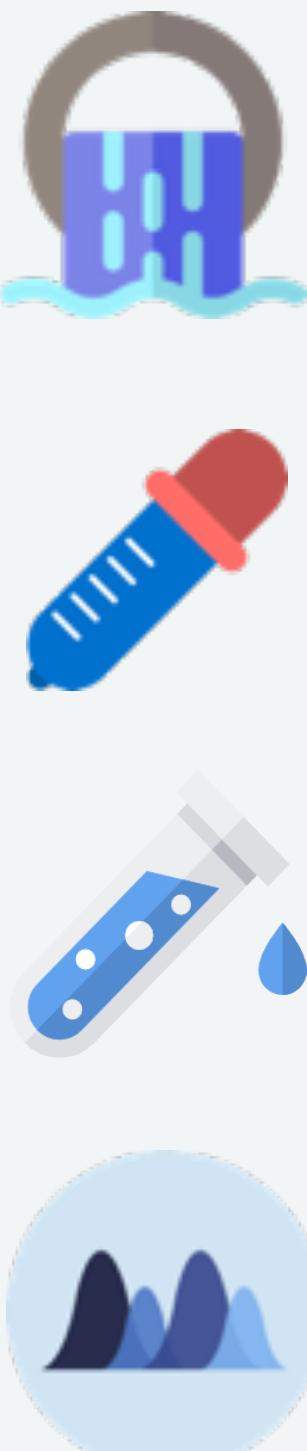
- To develop an **analytical procedure** to quantify biomarkers of exposure to selected PFRs in wastewater (WW)
- To investigate the **stability** of the target PFRs in wastewater
- To examine **temporal and geographical differences** in exposure

Target compounds

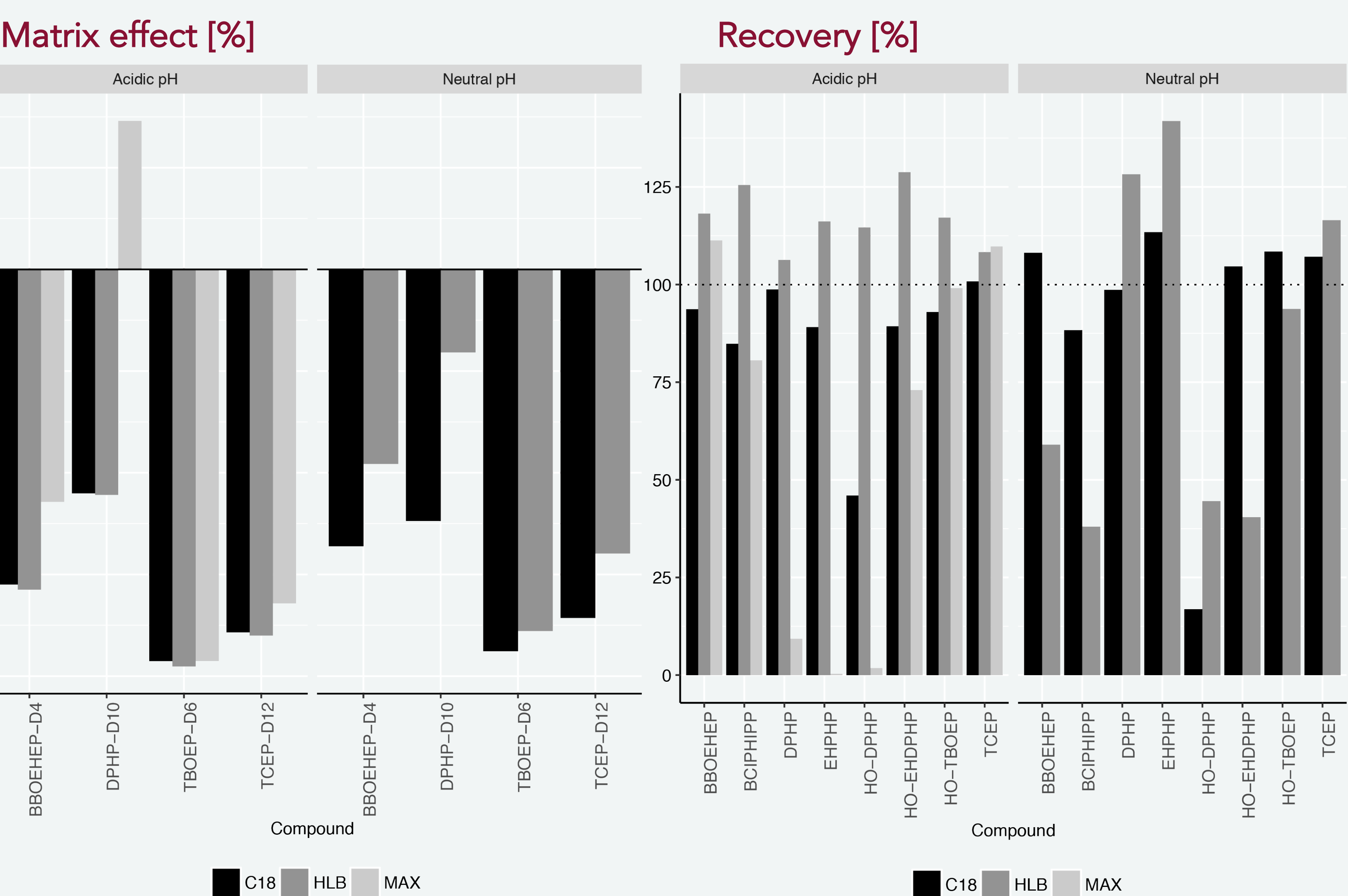
Parent PFR	Metabolites	Name
EHDPHP	HO-EHDPHP	2-ethyl-5-hydroxyhexyl diphenyl phosphate
	EHPHP	2-ethylhexyl phenyl phosphate
	DPHP	diphenyl phosphate
TBOEP	HO-TBOEP	bis(2-butoxyethyl) 3'-OH-2-butoxyethyl phosphate
	BBOEHEP	2-hydroxyethyl bis(2-butoxyethyl) phosphate
TCIPP	BCIPHIPP	1-hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate
	BCIPP	bis(1-chloro-2-propyl) phosphate
TPHP	DPHP	diphenyl phosphate
	HO-DPHP	4-hydroxyphenyl phenyl phosphate
	HO-TPHP	4-hydroxyphenyl diphenyl phosphate
TCEP	TCEP (*)	tris(chloroethyl) phosphate
	BCEP	bis(chloroethyl) phosphate

Sample preparation and analysis

- 100 mL WW sample spiked with (internal) **standards**
- Deconjugation with β -glucuronidase not necessary
- Centrifugation at 3000 g for 20 min
- Filtration through glass microfiber filters (1.6 μ m)
- Acidification of sample to pH 4-5
- SPE with **Bond-Elut C18** and acidic conditioning
- Elution with 5 mL of methanol
- Separation on Phenomenex Biphenyl (2.1x100 mm, 2.6 μ m)
- Analysis on Agilent 6460 LC-MS/MS
- Electrospray ionisation in +/- dynamic MRM mode



Results



Stability of compounds in wastewater

- PFR metabolites are relatively **stable** in over 24 hours at 4°C and 20 °C
- Addition of parent PFR compounds did not have substantial effects on PFR metabolite concentrations (not formed by microorganisms present in WW)
- Findings are in line with previous studies showing that **degradation of parent PFRs** in wastewater requires longer periods of time (i.e., days)
- Results support the hypothesis that levels of PFR metabolites measured in wastewater can be related to human exposure.

Monitoring Community-wide Exposure to PFRs

Per capita loads [mg day⁻¹ 1000 inhabitants⁻¹]

Compound	OST	LIER	GER	NIN
HO-DPHP	-	-	-	-
DPHP	21 - 23	57 - 83	170 - 175	17 - 18
BCIPHIPP	2.1 - 3.0	1.8 - 3.3	3.0 - 3.1	2.5 - 2.8
TCEP	48 - 50	90 - 106	94 - 108	52 - 58
EHPHP	38 - 49	315 - 396	306 - 307	74 - 89
BBOEHEP	8.4 - 11	19 - 35	6.9 - 7.4	8.2 - 7.2
TBOEP-OH	12.1 - 15.4	25 - 60	12 - 14	12 - 12
HO-EHDPHP	1.2 - 0.6	1.3 - 2.7	1.0 - 1.5	1.6 - 0.7

- Homogenous results between locations due to the **ubiquitous exposure** to PFRs
- Observed differences could be linked to the **typology of the sampled locations**, such as the degree of urbanisation or the proximity to industrial facilities
- First time** that HO-TBOEP, BBOEHEP and BCIPHIPP are measured in wastewater
- High concentrations of **DPHP, TCEP and EHPHP**
 - DPHP has other sources: used as plasticizer, microbial hydrolysis of TPHP, from industrial activities and can also be derived from other PFRs than TPHP.
 - TCEP not only due to human exposure, also from leakage from consumer goods
 - High concentrations of EHPHP likely reflect the high levels of exposure to EHDPHP (the main PFR found in food samples)
- Additional sampling** campaign ongoing to obtain more detailed insights about the existence of geographical and temporal features in population-wide exposure to PFRs.

References

- Been, F., Bastiaensen, M., et al., *Analytical Chemistry* 89.18 (2017): 10045-10053.
1. van der Veen, I. et al., *Chemosphere* 88.10 (2012): 1119-1153.
2. Van den Eede, N. et al., *Environmental International* 74 (2015): 1-8.