Mining the chemical information of urban wastewater – Monitoring exposure to phosphorus flame retardants and plasticizers

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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 biomonitoring, PFR metabolites can be measured in wastewater to assess exposure in the general population^{2,3}.

Community-wide exposure

Monitoring Community-wide Exposure to PFRs

Geographical features [Antwerp, Brussels, Athens, Geneva, Vilnius]



Emerging contaminants WWTP

Aims

- Assess geographical differences across five European WWTP's
- Investigate temporal trends over four consecutive years at one WWTP
- Compare to human biomonitoring data and production volumes
- Estimate per capita **average urinary concentrations** based on population normalised mass loads of PFR metabolites measured in wastewater

Target compounds

Parent PFR	Metabolites	Name
EHDPHP	HO-EHDPHP	2-ethyl-5-hydroxyhexyl diphenyl phosphate
	EHPHP	2-ethylhexyl phenyl phosphate
	DPHP	diphenyl phosphate
	BBOEP	bis(2-butoxyethyl 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
TCEP	TCEP (*)	tris(chloroethyl) phosphate
TDCIPP	BDCIPP	bis(1,3-dichloro-2-propyl) phosphate

- Antwerp & Brussels (BE) show similar results, as well as Geneva (CH)
- Overall low levels in Athens (GR) compared to other cities
- Uniform levels of DPHP at all locations because applied as plasticizer
- EHPHP highest per capita loads at all locations particularly Vilnius (LT), suspected use as plasticizer?

Temporal trends [1 week per year, 2013-2016, using Antwerp WWTP data]



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

• Substantial changes for most compounds

• TCEP: decreased production in EU

- TCIPP: increased use in replacement of TCEP (see BCIPHIPP)
- TBOEP: increased levels in dust (see BBOEHEP)

Estimating urinary concentrations using Monte Carlo simulations



Filtration through glass microfiber filters (1.6 µm)
Acidification of sample to pH 4-5

SPE with Bond-Elut C18 and acidic conditioning
Elution with 5 mL of methanol



- Concentrations generally 0.5-1 orders of magnitude higher (i.e., mean and median) compared to recent biomonitoring data
- In some cases concentrations were similar to the upper range measured in biomonitoring studies
- However, **uncertainty in simulation**: other excretion routes (e.g. faeces?), nonhuman sources, in-sewer stability (biofilms), and populations estimates

References

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