Mining the chemical information of urban wastewater - Monitoring human exposure to phosphorous flame retardants and plasticizers (PFRs)

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1. Introduction

Phosphorous flame retardants and plasticizers (PFRs) are increasingly used as additives in consumer products (e.g., furniture, textiles, electronics and paints) and are easily released to the environment [1]. Because of their ubiquity and the multiple exposure routes, they may pose a threat to human health. Potential health effects of certain PFRs include carcinogenicity, neurotoxicity, allergies and endocrine disruption [2]. At the individual level, exposure is generally assessed through the analysis of specific biomarkers in biological matrices. However, these studies are subject to various limitations: they require the collection of numerous samples from multiple individuals, can be expensive and logistically difficult to organise, often lack of temporal dimension (i.e., individuals being sampled only once or, at best, over a 24 h period) and suffer from selection bias. These issues are particularly important when it comes to monitoring population-wide exposure over space and time. In urban environments, human excretions (e.g., urine and faeces) are collected in sewer systems and conveyed to wastewater treatment plants (WWTPs). Wastewater (WW) can thus be seen as a pooled sample of excretions from a large population. In this perspective, mining the chemical information contained in WW could complement existing biomonitoring programs by gathering population-wide information about exposure to contaminants. The objective of the present work consisted in exploring the possibility of using urban WW as an alternative matrix to gain spatial and temporal information about community-wide exposure to PFRs.

2. Materials and methods

The present work focused on the analysis of selected biomarkers of exposure to PFRs (i.e., urinary phase I and phase II metabolites), namely: 2-ethyl-5-hydroxyhexyl diphenyl phosphate (HO-EHDPHP), 2-ethylhexyl phenyl phosphate (EHPHP) and diphenyl phosphate (DPHP), metabolites of 2-ethylhexyldiphenyl phosphate (EHDPHP); bis(2-butoxyethyl) phosphate (BBOEP), bis(2-butoxyethyl) 3′-hydroxy-2-butoxyethyl phosphate (HO-TBOEP) and 2-hydroxyethyl bis(2-butoxyethyl) phosphate (BBOEHEP), metabolites of tris(2-butoxyethyl) phosphate (TBOEP); 1-hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate (BCIPHIPP), metabolite of tris(2-chloroisopropyl) phosphate (TCIPP); diphenyl phosphate (DPHP) and hydroxyphenyl phenyl phosphate (HO-DPHP), metabolites of triphenyl phosphate (TPHP); bis(1,3-dichloroisopropyl) phosphate (BDCIPP), metabolite of Tris(1,3-dichloroisopropyl) phosphate (TDCIPP); di-n-butyl phosphate (DNBP), metabolite of tri-n-butyl phosphate (TNBP); tris(chloroethyl) phosphate (TCEP). Samples were collected at the influent of five WWTPs, in Antwerp (BE), Brussels (BE), Athens (GR), Geneva (CH) and Vilnius (LT). Samples were processed and analysed using our previously developed and validated method based on solid-phase extraction and liquid chromatography-tandem mass spectrometry [3]. Using a stochastic model for urine production and Monte Carlo methods, average urinary concentrations were estimated based on biomarker levels measured in WW.

3. Results and discussion

3.1. Occurrence of biomarkers in wastewater

Analyte concentrations ranged from 2124 ng L^{-1} for EHPHP to 2.9 ng L^{-1} for HO-EDHPHP. For some analytes, these levels are likely linked to their use as flame retardants and plasticizers (i.e., TCEP, DPHP, DNBP and likely EHPHP). Strong correlations (Spearman $\rho > 0.8$) were found between BBOEP, BBOEHEP and HO-TBOEP, all metabolites of TBOEP. Moderate to strong correlations were also found between DPHP, EHPHP and DNBP (Spearman $\rho > 0.4$). One hypothesis explaining these results could be that these

compounds share common sources, yet no clear information in this regard is available. Finally, moderate negative correlations (Spearman $\rho < -0.4$) were found between EHPHP and HO-EHDPHP, as well as the metabolites of TBOEP. These were partly attributed to the effect of stormwater runoff. In fact, EHPHP exhibited a positive correlation with flow rates (i.e., likely mobilized from outdoor surfaces or present in precipitation), whilst the contrary was the case for the other compounds.

3.2. Monitoring community-wide exposure to PFRs

Measured analyte concentrations were multiplied by flow rates and further divided by the catchment population to obtain population-normalised loads (in mg day^{-1} 1000 $inhabitants^{-1}$). Athens presented the lowest values for all compounds, except for EHPHP. High levels of EHPHP were measured in Vilnius, whilst other compounds were similar or lower compared to the other locations. Antwerp and Brussels had similar concentrations for most compounds. Nonetheless, differences were observed for DNBP and BDCIPP, both significantly higher in Antwerp compared to Brussels (Wilcox rank sum, *p*-value = 0.002 and 0.001, $\alpha = 0.05$, respectively). Although one could expect levels of these biomarkers to be relatively homogeneous, due to the ubiquity of PFRs, the obtained results suggest that, at least for some compounds, spatial differences in exposure may exist.

Temporal trends were investigated in WW samples collected from the city of Antwerp between 2013 and 2016. Substantial changes in levels of target chemicals could be observed over the investigated period. Specifically, a drop in population-normalised loads was observed since 2013 for DPHP, EHPHP and HO-EHDPHP. A significant decrease over the monitoring period was also observed for TCEP (Kruskal-Wallis rank sum test, *p*-value < 0.001). The observed decrease is in line with the declining use of TCEP in Europe since 2003 [4]. A steady increase in loads was on the other hand observed for BCIPHIPP, BDCIPP and BBOEHEP. Yet, these were statistically significant only for BCIPHIPP and BBOEHEP (Kruskal-Wallis rank sum test, *p*-value < 0.001). Increased use of TCIPP as the replacement of TCEP [5] could explain the observed rise in BCIPHIPP levels over the investigated period. Increasing levels of BDCIPP are in line with figures from the US which reported increasing concentrations in urine between 2003 and 2016. The obtained results suggest that WW analysis could provide highly relevant information about temporal changes in exposure at the population level. Based on biomarker levels measured in WW, average urinary concentrations were computed. Overall, these were found to be higher compared to results from human biomonitoring studies. For instance, median urinary concentrations of BDCIPP estimated from WW ranged from 3 to 11 ng mL^{-1}, whereas results from biomonitoring were generally below 1 ng mL^{-1}. Whilst uncertainties due to the calculation approach (i.e., lack of precise and dynamic data about the size of the population) or inputs from external sources cannot be excluded, these differences could also be linked to the fact that WW samples were collected over 24 h (cumulated average value), while spot urine samples (single value) are generally considered in human studies.

4. Conclusions

Whilst still at its infancy, monitoring human exposure to contaminants via WW analysis is highly compelling as it has the potential to deliver unique spatial and temporal data. This could be used to complement results from environmental (e.g., indoor and outdoor levels) and epidemiological (e.g., biomonitoring, health end-points and socio-economic factors) studies. Nonetheless, further research is needed, in particular to better understand in-sewer stability of the target compounds, as well as to conduct long-term sampling campaigns to investigate potential seasonal effects.

5. References

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