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Critical evaluation of monitoring strategy for the multi-residue determination of 90 chiral and achiral micropollutants in effluent wastewater

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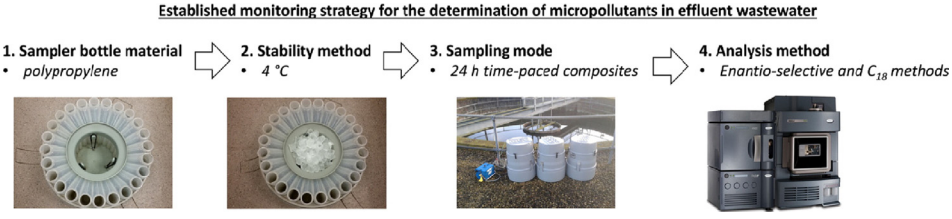
HIGHLIGHTS

- Polypropylene suitable as sampler bottle material for 89 of 90 micropollutants.
- Cooling composite samples to 4 °C stabilised ≥81 compounds in studied effluents.
- Time composites gave similar concentration data to volume composites in effluent.
- Little diurnal variability in enantiomeric distribution of chiral micropollutants.

GRAPHICAL ABSTRACT



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ABSTRACT

It is essential to monitor the release of organic micropollutants from wastewater treatment plants (WWTPs) for developing environmental risk assessment and assessing compliance with legislative regulation. In this study the impact of sampling strategy on the quantitative determination of micropollutants in effluent wastewater was investigated. An extended list of 90 chiral and achiral micropollutants representing a broad range of biological and physico-chemical properties were studied simultaneously for the first time. During composite sample collection micropollutants can degrade resulting in the under-estimation of concentration. Cooling collected sub-samples to 4 °C stabilised ≥81 of 90 micropollutants to acceptable levels (±20% of the initial concentration) in the studied effluents. However, achieving stability for all micropollutants will require an integrated approach to sample collection (i.e., multi-bottle sampling with more than one stabilisation method applied). Full-scale monitoring of effluent revealed time-paced composites attained similar information to volume-paced composites (influent wastewater requires a sampling mode responsive to flow variation). The option of monitoring effluent using time-paced composite samplers is advantageous as not all WWTPs have flow controlled samplers or suitable sites for deploying portable flow meters. There has been little research to date on the impact of monitoring strategy on the determination of chiral micropollutants at the enantiomeric level. Variability in wastewater flow results in a dynamic hydraulic retention time within the WWTP (and upstream sewerage system). Despite chiral micropollutants being susceptible to stereo-selective degradation, no diurnal variability in their enantiomeric distribution was observed. However, unused medication can be directly disposed into the sewer network creating short-term (e.g., daily) changes to their enantiomeric distribution. As enantio-specific toxicity is observed in the environment, similar resolution of enantio-selective analysis to more routinely applied achiral methods is needed throughout the monitoring period for accurate risk assessment.

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1. Introduction

The presence and possible impact of municipally derived organic micropollutants in the environment is of increasing concern. Several micropollutants have been recommended for inclusion in a watch list under the Water Framework Directive (2000/60/EC) (Carvalho et al., 2015). This includes diclofenac, estrone, 17β-estradiol, 17α-ethinylestradiol, erythromycin, clarithromycin, and azithromycin. Diclofenac, 17β-estradiol and 17α-ethinylestradiol have proposed Environmental Quality Standards (EQS, expressed as annual average) of 100, 0.4 and 0.035 ng L^{-1}, respectively (European Commission, 2012). Consequently, it is expected that legislation will be implemented to govern the discharge of these types of micropollutants from wastewater treatment plants (WWTPs) into the environment. Developing environmental legislation is underpinned by robust monitoring data-sets and accurate risk assessment. However, such data-sets (previously limited by analytical capabilities) are currently lacking due to inadequate sampling protocols.

Composite sampling is usually applied to obtain average micropollutant concentrations over 24 h. An uncertainty associated with this approach is the loss of micropollutants during sample collection (McCall et al., 2016). Micropollutants could be lost due to sorption onto sampler bottles. Polypropylene is considered the most widely used sampler bottle material, yet there is a paucity of information published in the literature on the loss of micropollutants from water to its surface. Micropollutants can also be degraded by bacteria present within the wastewater matrix (Hillebrand et al., 2013). Cooling sub-samples to 4 °C, adjusting to pH 2 and adding sodium azide have all been suggested to improve stability (Baker and Kasprzyk-Hordern, 2011; Vanderford et al., 2011; Hillebrand et al., 2013). To date these different stabilisation methods have not been challenged with a high number of micropollutants (>50), representing a broad range of biological and physico-chemical properties. Ideally, a generic stabilisation method could be established for the multi-residue determination of micropollutants in wastewaters.

Ort et al. (2010) showed that collecting a time proportional composite sample with a sampling frequency of ≤20 min can give inaccurate/biased results in influent wastewater for some micropollutants. This was established through a modelling study which found a composite sampling approach that is responsive to variations in wastewater flow (flow or volume proportional) is needed to give unbiased information (depending on the sampling frequency and number of toilet flushes or 'pulses' (p) expected per micropollutant in the catchment each day) (Ort et al., 2010). It is currently unknown whether these observations are applicable to effluent wastewater. Mixing within the WWTP will provide a more uniform flow and concentration profile. On the other hand this may be counteracted by variability in micropollutant degradation due to dynamic wastewater flow and secondary treatment hydraulic retention time (HRT) (Majewsky et al., 2011). This is essential to investigate to ensure current sampling practices of effluent wastewater obtain accurate concentration information. Not all WWTPs have permanently deployed flow dependent samplers (particularly at smaller sites serving a population of ≤100,000), and rely on portable time dependent samplers for monitoring micropollutants. To date, there is a paucity of information on the impact of active sampling mode to the quantitative determination of micropollutants in effluent wastewater.

Obtaining accurate information on the enantiomeric distribution of chiral micropollutants is essential for accurate environmental risk assessment and needs incorporated into monitoring strategies (Petrie et al., 2014). Enantiomers of the same chiral micropollutant can exert different toxicological responses to exposed aquatic species (Stanley et al., 2007; De Andrés et al., 2009). However, little is known of the temporal variability in enantiomeric distribution of chiral micropollutants in effluent during a typical one-week monitoring period. As many chiral micropollutants undergo stereo-selective degradation, enantiomeric distribution could change with varying in-sewer and WWTP HRT. Such influences are expected to be compound specific as different chiral micropollutants undergo varying degrees of stereo-selectivity when exposed to environmental conditions (Kasprzyk-Hordern and Baker, 2012).

The aim of this study was to evaluate the impact of monitoring strategy on the quantitative determination of micropollutants in effluent wastewater. This will help inform the design of future environmental monitoring studies for improved data quality to improve risk assessment and assess compliance to environmental regulation. The objectives of the study were to:

i. Assess the behaviour of 90 micropollutants during composite sample collection using a range of stabilisation methods
ii. Compare grab sampling, and volume- and time- paced composite sampling for the determination of micropollutants in effluent with a wide range of expected pulses
iii. Evaluate diurnal changes in enantiomeric distribution of chiral micropollutants in effluent wastewater

A total of 90 micropollutants representing a broad range of biological and physico-chemical properties were studied (Table S1), and both concentration and EF (where possible) were determined. This is the first study which has investigated the impact of sampling strategy on such a high number of diverse micropollutants (including enantiomerism) simultaneously in effluent. Equivalent studies were also conducted in influent wastewater for comparison purposes and full findings of these can be found in Supplementary Material.

2. Materials and methods

2.1. Materials

Information on studied micropollutants are detailed in Table S1. Internal standards acetaminophen-D4, ibuprofen-D3, bisphenol A-D16, carbamazepine-13C6, ketoprofen-D3, naproxen-D3, sertraline-D3, tamoxifen 13C2 15N, propranolol-D7, atenolol-D5 and metformin (dimethyl-D6) were purchased from Sigma-Aldrich (Gillingham, UK). Bezafibrate-D6 was obtained from QMX laboratories (Thaxted, UK). Methylparaben-13C, amphetamine-D5, methamphetamine-D5, MDMA-D5, 3,4-methylenedioxy-amphetamine-D5 (MDA-D5), heroin-D9, codeine-D6, ketamine-D4, cocaine-D3, benzoylecgonine-D8, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine-D3 (EDDP-D3), morphine-D3, cotinine-D3, cocaethylene-D8, temazepam-D5, 1S,2R-(+)-ephedrine-D3, mephedrone-D3, methadone-D9, norketamine-D4, estrone (2,4,16,16-D4), estradiol (2,4,16,16-D4) and quetiapine-D8 hemifumurate were purchased from LGC standards (Middlesex, UK). Citalopram-D6, metoprolol-D7, fluoxetine-D5 and mirtazapine-D3 were obtained from TRC (Toronto, Canada). Methanol (MeOH) and toluene was HPLC grade and purchased from Sigma-Aldrich. Water (H_2O) was of 18.2 MΩ quality (Elga, Marlow, UK). All glassware was deactivated using 5% dimethylchlorosilane (DMDCS) in toluene (Sigma–Aldrich). Ammonium acetate (NH_4OAc), ammonium fluoride, sodium azide (NaN_3), ammonium hydroxide (NH_4OH), hydrochloric acid (HCl), formic acid (HCOOH) and acetic acid (1.0 M) were purchased from Sigma-Aldrich (Gillingham, UK). Oasis HLB (60 mg, 3 mL) solid phase extraction (SPE) cartridges were purchased from Waters (Manchester, UK).

2.2. Analytical methods

Briefly, samples for SPE were brought to room temperature, filtered (GF/F 0.7 μm glass fibre) and 50 mL aliquots spiked with 50 ng of all internal standards. These were loaded onto pre-conditioned Oasis HLB cartridges, dried and eluted using 4 mL MeOH. If SPE cartridges were frozen prior to elution, they were eluted and analysed within one

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