Markers of anthropogenic contamination: A validated method for quantification of pharmaceuticals, illicit drug metabolites, perfluorinated compounds, and plasticisers in sewage treatment effluent and rain runoff

John L. Wilkinson [a], [*], Julian Swinden [b], Peter S. Hooda [a], James Barker [b], Stephen Barton [b]

[a] School of Natural and Built Environments, Kingston University London, Kingston-upon-Thames, Surrey, United Kingdom
[b] School of Life Sciences, Pharmacy and Chemistry, Kingston University London, Kingston-upon-Thames, Surrey, United Kingdom

HIGHLIGHTS

- SPE HPLC-MS/MS method developed and validated for detection of 13 PPCPs/ECs.
- Mean levels in STW effluents from 3.6 ng/L (ethinylestradiol) to 210.2 ng/L (BPA).
- PFCs/plasticisers in street runoff up to 8.5 times more concentrated than STW eff.
- Mean analyte loads ranged from 0.2 to 6.1 g/day (benzoylecgonine, BPA) in STW eff.

ARTICLE INFO

ABSTRACT

An effective, specific and accurate method is presented for the quantification of 13 markers of anthropogenic contaminants in water using solid phase extraction (SPE) followed by high performance liquid chromatography (HPLC) tandem mass spectrometry (MS/MS). Validation was conducted according to the International Conference on Harmonisation (ICH) guidelines. Method recoveries ranged from 77 to 114% and limits of quantification between 0.75 and 4.91 ng/L. A study was undertaken to quantify the concentrations and loadings of the selected contaminants in 6 sewage treatment works (STW) effluent discharges as well as concentrations in 5 rain-driven street runoffs and field drainages. Detection frequencies in STW effluent ranged from 25% (ethinylestradiol) to 100% (benzoylecgonine, bisphenol-A (BPA), bisphenol-S (BPS) and diclofenac). Average concentrations of detected compounds in STW effluents ranged from 3.62 ng/L (ethinylestradiol) to 210 ng/L (BPA). Levels of perfluorinated compounds (PFCs) perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) as well as the plasticiser BPA were found in street runoff at maximum levels of 1160 ng/L, 647 ng/L and 2405 ng/L respectively (8.52, 3.09 and 2.7 times more concentrated than maximum levels in STW effluents respectively). Rain-driven street runoff may have an effect on levels of PFCs and plasticisers in receiving rivers and should be further investigated. Together, this method with the 13 selected contaminants enables the quantification of various markers of anthropogenic pollutants: *inter alia* pharmaceuticals, illicit drugs and their metabolites from humans and improper disposal of drugs, while the plasticisers and perfluorinated compounds may also indicate contamination from industrial and transport activity (street runoff).

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1. Introduction

From the turn of the 21st century, the occurrence, fate and environmental toxicity of pharmaceuticals and other so-called emerging contaminants in the aquatic environment (rivers, reservoirs, oceans and drinking water) has been the subject of many studies (e.g., Kolpin et al., 2002; Vajda et al., 2008, 2011; Llorca

* Corresponding author. Kingston University London, Penrhyn Road Main Building, Room 2021, Kingston-upon-Thames, Surrey, United Kingdom.
E-mail address: j.wilkinson@kingston.ac.uk (J.L. Wilkinson).

et al., 2012; King et al., 2015) and reviews (e.g., Petrie et al., 2015; Wilkinson et al., 2015). Nearly every human and veterinary pharmaceutical has been detected in the aquatic environment, typically at sub-μg/L concentrations. Evidence suggests that once in the aquatic environment, residues of some pharmaceuticals and other emerging contaminants (ECs) cause biological disruption/dysfunction in exposed non-target organisms via mechanisms such as endocrine dysfunction (Woodling et al., 2006; Vajda et al., 2008, 2011; Patisaul and Adewale, 2009; Vajda et al., 2011). Once administered, pharmaceuticals are rarely, if ever, completely metabolised in the body and are directed to sewage treatment works (STWs) via urinary and biliary fecal excretions (Ijemba, 2006; Silva et al., 2011). Residues of pharmaceuticals typically enter the aquatic environment through STW effluent outfalls where many compounds do not completely degrade (Verlicchi et al., 2012). Other anthropogenic contaminants such as musk compounds used in fragrances and lotions, surfactants, and ultraviolet filters in sunscreen are also directed to STWs via wastewater (Peck, 2006; Roosens et al., 2007). Supplementary Table 1 shows concentrations of 21 pharmaceuticals and other emerging contaminants which are typically detected in river water.

Emerging contaminants are commonly defined as any compound (both synthetic and natural) in the environment whose presence is not routinely monitored and shows the potential to cause ecological disruption (Raghav et al., 2013; United States Geological Survey, 2014). Among such ECs are perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorobutane sulfonic acid (PFBS), and perfluorooctane sulfonate (PFOS) as well as plasticisers including bisphenol-A (BPA) and bisphenol-S (BPS) among others. Plasticisers are commonly used to modify the rigidity of plastic materials and are used in product and food packaging, manufacture of polycarbonate plastic, thermal receipt paper, water pipes, epoxy resins, vinyl floors, car tires, among many others (U.S. Food and Drug Administration, 2015). Perfluorinated compounds are commonly used in waterproofing agents, polishes, waxes, non-stick cookware and cleaning products (Posner, 2012). ECs such as plasticisers and PFCs are also known to enter the aquatic environment through STW effluent outfalls (Meyer and Bester, 2004; Zhang et al., 2013).

Biodegradation of PFC precursor molecules during sewage treatment into other PFCs is suggested to increase their effluent concentrations by 32–290 times over that in the influent (Zhang et al., 2013). For example, Zhang et al. (2013) reported that of 28 sampled STWs in economically developed areas of China, effluent concentrations of PFOA were higher than influent 81% of the time, 69% of the time for perfluorononanoic acid (PFNA), 57% of the time for perfluorobutane sulfonic acid (PFBS) and 58% of the time for PFOS. Precursor molecules found in STW influent include N-ethyl perfluorooctane sulphonamide, which degrades into PFOS and fluorotelomer alcohols (e.g., 8:2 fluorotelomer alcohol) which degrade into PFOA (Zhang et al., 2013; Avendaño and Liu, 2015).

Recent evidence indicates that PFCs may be introduced into the aquatic environment through non-point sources, such as runoff from streets (Zushi et al., 2008; Murakami et al., 2009; Furl et al., 2011). Zushi et al. (2008) reported concentrations of PFCs 2–11 times higher in rain runoff than in the effluent outfalls of three studied STWs along the Tsurumi River (Yokohama City, Kanagawa Prefecture, Japan). Despite evidence of PFCs introduced to the aquatic environment through runoff, there are limited studies quantifying similar contributions of other ECs, such as plasticisers. Furthermore, studies comparing STW effluent to runoff contributions of PFCs and plasticisers into the same river system is limited.

Here, a validated method is presented to accurately and specifically quantify 13 markers of anthropogenic contamination in fresh water: *inter alia* pharmaceuticals, illicit drugs and their metabolites. Pharmaceuticals and illicit drugs are specific indicators of human-derived contamination and improper disposal of drugs, while the plasticisers and perfluorinated compounds also indicate contamination from industrial and transport activity (street runoff). The presented method can be used to efficiently and specifically quantify concentrations of contaminants of human, industrial and transportation origins. A key feature of this method is the achievement of adequate detection limits using a relatively small amount of water (200 mL) for analysis. Here, increased ease of sample transport (due to the small volume of water required) enables analysis of a greater number of samples in relatively little time. The sensitivity/detection limits of the method proposed as such can be further increased by increasing the amount of sample water used in solid phase extraction (SPE). The developed method enabled a comparison between contaminant inputs into selected rivers via sewage treatment effluent and runoff from both streets and fields.

2. Materials and methods

2.1. Standards and reagents

Thirteen compounds were selected for analysis including pharmaceuticals: ethinylestradiol, acetaminophen and diclofenac, illicit drugs and metabolites: methamphetamine and its metabolite amphetamine and benzoylecgonine (metabolite of cocaine), plasticisers: bisphenol-S (BPS), bisphenol-A (BPA) and its biotransformation product 4′-hydroxyacetophenone (HAP), perfluorinated compounds: PFOA, PFOS, PFNA, and PFBS, and deuterated internal standards: BPA-D16, acetominophen-D4 and methamphetamine-D5. All compounds were purchased from Sigma Aldrich (Gillingham, Dorset, U.K.) and were of 96% purity or higher. PFOS was purchased as a potassium salt and benzoylecgonine was tetrahydrated. Strata-X 33 μm polymeric reversed phase 200 mg/6 mL SPE cartridges were purchased from Phenomenex (Macclesfield, Cheshire, U.K.). A Phenomenex Kinetex 2.6u C18 150 × 2.1 mm chromatography column using a SecurityGuard ULTRA UHPLC C18 2.1 mm guard column was purchased from Phenomenex (Macclesfield, Cheshire, U.K.). Whatman GF/F-grade glass microfiber filters (diameter 47 mm, pore size 0.7 μm) were purchased from Fisher Scientific (Loughborough, Leicestershire, U.K.).

Stock solutions were prepared for each compound and internal standards at a concentration of 1000 mg/L in LCMS-grade acetonitrile except for PFOS, diclofenac and ethinylestradiol, which were prepared at 1000 mg/L in HPLC grade acetone. A mixed solution was made in LCMS-grade acetonitrile to a concentration of 5 mg/L for all analytes except BPA at 30 mg/L, ethinylestradiol at 25 mg/L, and HAP at 7.5 mg/L which was further diluted into working solutions. Concentrations of target analytes in the mixed solution were optimised based on spectrometer sensitivity to each respective compound. Solutions were stored in 10 mL borosilicate glass volumetric flasks at 4 °C in the dark and renewed monthly. A mixture of all compounds at 100 ng/L was analysed via HPLC-MS/MS once per week for 4-weeks to ensure no significant degradation occurred during monthly use of standard solutions.

2.2. Sample collection

Effluent samples (n = 12) were collected in duplicate from six STWs along three rivers in the south east of England (Hogsmill, Bourne and Blackwater: Supplementary Table 2). Runoff samples were collected from grass field drainage (n = 3) and street runoff (n = 2) during periods of rainfall (Supplementary Table 3).

Grab samples were collected (200 mL) in amber glass bottles. All