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Analysis of emerging contaminants in water and solid samples using high resolution mass spectrometry with a Q Exactive orbital ion trap and estrogenic activity with YES-assay

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HIGHLIGHTS

- We analyzed 31 emerging contaminants in water, suspended particulates and sediments.
- Solid-liquid partitioning coefficient (K_d) are reported for 12 compounds.
- No clear relationship observed between chemical measurements and YES assay results.

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ABSTRACT

Trace emerging contaminants (ECs) occur in both waste and surface waters that are rich in particulates that have been found to sorb several organic contaminants. An analytical method based on off-line solid-phase extraction (SPE) followed by liquid chromatography-mass spectrometry (LC-MS) analysis was developed for the detection and quantification of 31 ECs from surface water, wastewater, suspended particulate matter (SPM) as well as sediments. Lyophilized sediments and air-dried SPM were subjected to ultrasonic extraction. Water samples and extracts were then concentrated and cleaned-up by off-line SPE. Quantification was realized using a Q Exactive mass spectrometer in both full scan (FS) and MS^2 modes. These two modes were optimized and compared to determine which one was the most suitable for each matrix studied. Yeast estrogen screen assay (YES-assay) adapted from the direct measurement of estrogenic activity without sample extraction was tested on filtered wastewater samples. An endocrine disrupting effect was detected in all effluent samples analyzed with estradiol equivalent concentrations ranging from 4.4 to 720 ng eq E2 L^{-1} for the WWTP-1 and 6.5–42 ng eq E2 L^{-1} for the WWTP-2. The analytical methods were also applied on six samples of surface water, the corresponding SPM, the sediments and thirty-nine effluent samples from two wastewater treatment plants (WWTPs) sampled over a period of five months (February to June 2014).

1. Introduction

Urban sanitary wastewaters are a recognized source of contaminants of emerging concern (Lapworth et al., 2012; Luo et al., 2014) which are often shortened to “emerging contaminants” (ECs) (Sauvé and Desrosiers, 2014). Such ECs in wastewaters are of different origins: pharmaceuticals, hormones (both synthetic and natural), personal care products, disinfectants, drugs of abuse, plasticizers, pesticides, insect repellents, sun screens, surfactants, antiadhesives and many others. We can expect to find this whole suite of compounds as the original product but many will also appear as their transformation products and we cannot simply seek

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the parent compounds. Many transformation products could still have some significant biological activity and can act as endocrine disruptors (EDCs) and as such, could have significant impacts on fish, amphibian or other exposed populations (Fent et al., 2006; Pomati et al., 2006; Burkhardt-Holm, 2010). If present in urban wastewater effluents, these compounds are continually introduced to the receiving aquatic environment. Their presence comes from an incomplete degradation or removal through wastewater treatment plants (WWTPs), defective septic systems, leaking underground sewage, and surface run-off or directly via release from the skin during swimming, bathing or showering (Burkhardt-Holm, 2010; Ratola et al., 2012). The presence of ECs in the environment (at trace concentrations, ranging from a few ng L^{-1} to several μg L^{-1}) has become an emerging issue since little is known about the long term risk and the potential ecological or human health risk associated with chronic exposure to trace levels of multiple chemicals compounds (Stackelberg et al., 2004). Analysing the effluents of wastewater treatment plants allows the quantification of the environmental release of such emerging contaminants into receiving water bodies. It can also be used to estimate drug consumption (Lai et al., 2013), to measure the removal efficiency of WWTP (Martin et al., 2012) or to better understand the toxicity of wastewater effluents (Smital et al., 2011). However, most of the published data on the analysis of ECs in WWTPs focus on dissolved water concentrations and often neglect the fraction of contaminants that is associated with suspended particulate matter (SPM) (Gracia-Lor et al., 2012; Fayad et al., 2013; Lai et al., 2013; Ferrando-Climent et al., 2014).

However, wastewaters are characterized by the presence of SPM in different amounts, which have been found to contain a significant proportion of ECs (Baker and Kasprzyk-Hordern, 2011b; Barco-Bonilla et al., 2013). The lack of information on the solid-bound fraction of contaminants in wastewater could lead to an underestimation of the concentration and overall releases of several compounds. Considering that wastewaters are a complex multiphase matrix allows a better mass balance and a better understanding of the fate of the ECs during all stages of the wastewater-treatment process and the transformations into the receiving water. Our objective is to propose a multi-residue analytical method to detect and quantify a panel of suspected or known EDCs in the wastewater effluents, surface waters, sediments and SPM from surface water and WWTPs, targeting: steroidal hormones (estradiol, estriol, estrone, levonorgestrel, norethindrone, ethinylestradiol, progesterone, testosterone), pharmaceuticals and personal care products (PPCPs) (caffeine, carbamazepine, desvenlafaxine, venlafaxine, diazepam, fentanyl, norfentanyl, oxazepam, tamoxifen, sulfamethoxazole, diclofenac, fluoxetine), illicit drugs along with their main metabolites (cocaine, benzoylecgonine, MDMA, mephedrone, methylephedrine), two sterols (cholesterol and coprostanol), a herbicide and its metabolite (atrazine, desethylatrazine), a plastic by-product (bisphenol A) and a preservative agent (methylparaben). Selected chemical properties of each molecule are presented in Table 1. The presence of these 31 molecules in different matrices has been shown in different studies using different analytical techniques (Bijlsma et al., 2009; Sánchez-Avila et al., 2009; Martín et al., 2010; Metcalfe et al., 2010; Baker and Kasprzyk-Hordern, 2011b; Daneshvar et al., 2012; Gracia-Lor et al., 2012; Rúa-Gómez and Püttmann, 2012; Andrási et al., 2013; Barco-Bonilla et al., 2013; Campo et al., 2013; Fayad et al., 2013; Mwenesongole et al., 2013; Yuan et al., 2013; Darwano et al., 2014; Ferrando-Climent et al., 2014; Kostich et al., 2014; Álvarez-Ruiz et al., 2015; Vergeynst et al., 2015). Nevertheless, only a few methods allow the simultaneous quantification of series of compounds with such a range of physicochemical properties in different matrices.

To date, the instrument of choice for the analysis of ECs in complex matrices is based on liquid or gas chromatography coupled to tandem mass spectrometry (MS/MS). However gas chromatography (GC) methods usually require a primary treatment for high molecular weight and low-volatility compounds, thus liquid chromatography (LC) was preferred – especially to integrate many polar compounds which are resilient to GC methods. Moreover, the triple quadruple (QqQ) is certainly one of the most used type of mass spectrometer allowing sensitivity and selectivity advantage with the multiple reaction monitoring (MRM) (Kaufmann et al., 2010). However, the QqQ could not distinguish precisely a target compound and an interfering compound within a decimal difference, and thus could generate false positive. It has been demonstrated that the selectivity and reliability of the detection process of a high resolution mass spectrometer exceeds the performance of a tandem mass spectrometer at a resolution of 50,000 full width at half maximum (FWHM) and at corresponding mass windows (Kaufmann et al., 2010; Fedorova et al., 2013). Thus to improve performances, we used an Orbitrap-based orbital ion trap high resolution mass spectrometer, a Q Exactive (Thermo Fisher Scientific, Waltham, MA) with resolving power up to 140, 000 FWHM at m/z 200. Furthermore, the Q Exactive system combines the Orbitrap with a high-performance quadruple and high-energy collisional induced dissociation (HCD) cell which allows the possibility of precursor ion fragmentation providing high sensitivity and selectivity – in a manner not unlike what can be performed using tandem mass spectrometry. The aim of this study was to develop a sensitive and selective multi-residue analytical method for a wide range of compounds in different matrices with the use of a SPE sorbent allowing different retention processes and multiple elution steps with different organic solvents. The Q Exactive analyses were carried out in two different modes: full-scan MS and targeted MS/MS (MS^2) using a polarity-switching atmospheric pressure chemical ionization source (APCI), allowing acquisition of all analytes in a single run. A mobile phase for the separation step, containing ammonium bicarbonate (NH_4HCO_3), has proven useful for the optimal ionisation in both positive and negative mode. After development and validation, the method was successfully applied to sediments, surface waters, wastewater effluents samples and SPM coming from two different wastewater treatment plants along the St. Lawrence River, in the province of Québec, Canada.

Chemical measurements can only provide the concentrations of endocrine disruptors, the actual effects and impacts will vary according to the target biological species or mechanisms studied and chemical measurements cannot integrate potential interactions of EDCs. To better accommodate such limitations, we have chosen to also evaluate the performance of a Yeast estrogen screen assay (YES-assay) adapted for direct measurement of estrogenic activity without sample extraction (Balsiger et al., 2010). This method can represent a rapid and potentially sensitive screening method for EDCs from wastewater for surveillance or monitoring projects and would hopefully help interpret the results.

2. Materials and methods

2.1. Sample collection and preparation

Wastewater effluent samples were collected each week in clean amber glass bottles from WWTP facilities along the St. Lawrence River (Quebec, Canada) i.e. WWTP-1 and WWTP-2 for a period of 5 months. Surface water samples were collected in the St. Lawrence River with clean amber glass bottles upstream and downstream of the WWTP-1 and in the overflow area for WWTP-2 in September 2014. All samples were taken in duplicate and filtered through 47 mm fiberglass filters (0.3 μm, Sterlitech, Kent, WA) previously