Science of the Total Environment 511 (2015) 319–330

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Analysis of drugs of abuse by online SPE-LC high resolution mass spectrometry: Communal assessment of consumption

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HIGHLIGHTS

- Online-SPE-LC–HRMS analysis of 18 illicit drugs and metabolites in sewage influents
- Positive detection of 14 drugs of abuse and metabolites in a college campus setting
- Consumption estimates were determined for amphetamine, THC, cocaine, and heroin.

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 16 December 2014
Accepted 16 December 2014
Available online xxxx

Editor: D. Barcelo

Keywords:
Illicit drugs
Online-SPE
High resolution mass spectrometry
College campus
Sewage influents

ABSTRACT

An online SPE-LC–HRMS method was developed to monitor the consumption of 18 drugs of abuse (DOAs) including amphetamines, opioids, cocainics, cannabinoids, lysergics, and their corresponding metabolites in a well characterized college campus setting via wastewater analysis. Filtered and diluted (10×) sewage water samples (5 mL inj.) were automatically pre-concentrated and analyzed in 15 min using a Thermo EQuan MAX online SPE system equipped with a HyperSep™ Retain PEP (20 × 2.1 mm × 12 μm) SPE column and a Hypersil Gold™ aQ (150 × 2.1 mm × 3 μm) analytical column. A Q Exactive™ Hybrid Quadrupole-Orbitrap HRMS was used in full scan mode ($R = 140{,}000$) for positive identification, and quantitation of target compounds. Method detection limits for all analytes ranged between 0.6 and 1.7 ng/L in sewage. A total of 14 DOAs were detected from two different locations (dorms and main college campus) within a one-year period. Most frequently detected drugs throughout the entire study were amphetamine (>96%) and THC's metabolite 11-nor-9-carboxy-Δ-9-THC (>100%) with maximum concentrations of 5956 and 2413 ng/L respectively. Daily doses per 1000 people were determined in order to assess consumption of THC, amphetamine, heroin and cocaine, in both dorms and main campus.

1. Introduction

Every year, the United Nations Office on Drugs and Crime (UNODC) generates a comprehensive report on the latest developments in drug markets, covering production, trafficking, consumption, and health consequences (UNODC, 2014). In the year 2012, the US alone reached its highest levels of illicit drug use in the past 10 years (16% of the population 12 years and older), with consumption being the greatest among those in their late teens or early twenties, as noted in the World Drug Report 2014 (UNODC, 2014). These figures, however, are not evaluated fast enough to provide real time understanding of the situation for law enforcement officials to take appropriate timely actions.

Multiple studies have reported wastewater-derived figures for the consumption of drugs of abuse (illicit and prescription drugs), as they provide a nonintrusive way to quickly assess social trends, usage patterns, and drug prevalence at the community level (Castiglioni et al., 2006; Zuccato et al., 2008; Chiaia and Banta-green, 2008; Huerta-Fontela et al., 2008; Bartelt-hunt et al., 2009; Boleda et al., 2009; Postigo et al., 2010; Baker and Kasprzyk-hordern, 2011; Nuijs et al., 2011; Bijlsma et al., 2012; Kasprzyk-Hordern and Baker, 2012). This in contrast to the more conservative, time-consuming, and intrusive approaches of social surveys, drug seizures, crime statistics, and medical examiner reports (Nuijs et al., 2009d; Baker and Kasprzyk-hordern, 2011; Burgard et al., 2013).

Besides the social, health, and economic implications illicit drugs pose, there is also the impact that these drugs could inflict over aquatic environments. For instance, Parolini et al. reported that exposure to 0.5 μg/L and 1 μg/L of cocaine (benzoylecgonine) caused oxidative stress in freshwater bivalve *Dreissena polymorpha*, due to imbalances of the enzyme defense chain (Parolini et al., 2013). Similarly to pharmaceuticals, illicit drugs are metabolized in the body and excreted in their unchanged form or as

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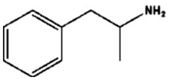
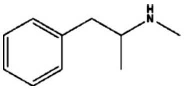
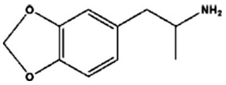
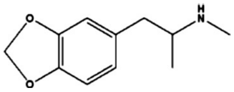
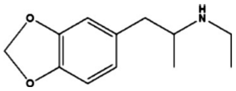
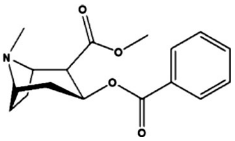
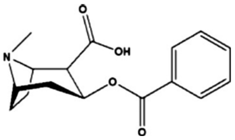
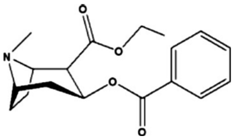
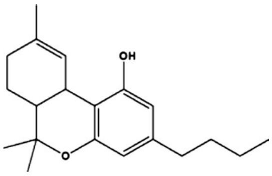
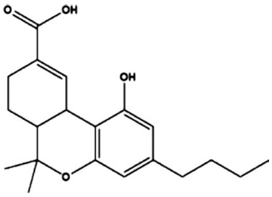
http://dx.doi.org/10.1016/j.scitotenv.2014.12.043
0048-9697/

their metabolite(s) reaching water streams (Hummel et al., 2006; Castiglioni et al., 2011; González-Mariño et al., 2012). Moreover, inadequate human disposal of these drugs increases their load and frequency of exposure to the environment, posing possible detrimental effects due to their unknown persistence and ecotoxicity (González-Mariño et al., 2012; Jurado et al., 2012; Valcárcel et al., 2012; Pal et al., 2013). This group of emerging contaminants as initially recognized by Petrovic and Richardson is typically assessed via analysis of effluent sewage and surface waters; and includes (but is not limited to) parent and metabolites of cocainics, amphetamine like stimulants (ALS), cannabinoids, and opiates (Petrovic et al., 2008; Richardson, 2008).

Solid phase extraction (SPE) has been the technique of choice for pre-concentration of illicit drugs in off-line applications. However, offline SPE is time consuming and requires multiple manual sample preparation steps decreasing sample throughput. Despite associated problems such as the need of careful method development for carryover control, online SPE has been gaining popularity for large environmental monitoring efforts as it provides minimal preparation steps, reduced reporting times and lower solvent usage relative to offline techniques (Batchu et al., 2013; Gorga et al., 2013; Panditi et al., 2013; Wang and Gardinali, 2013; Ramirez et al., 2014). Although studies using online SPE have been reported in the analysis of illicit drugs in sewage matrices, cannabinoids (one of the most consumed drugs) are only included in two of these methods which still required a separate pre-concentration protocol or suffered from poor sensitivity (Postigo et al., 2008; Fontanals et al., 2013; Ostman et al., 2013; Repice et al., 2013).

From the initial report of analysis of illicit drugs in sewage waters documented by Zuccato et al. in 2005, most analyses of DOAs have been performed using liquid chromatography coupled to MS or MS/MS detection, the latter typically involving triple quadrupole instruments operating in

Table 1
Structures, elemental formula, exact mass, mass error, pKa, Log Kow, and internal standard used for quantitation of target analytes.

Class	Analyte	Structure	Formula	Exact Mass	Mass Error (ppm)	pK_a[a]	Log Kow[b]	Internal Standard
Amphetamine-like compounds (ALCs)	Amphetamine (AM)		$C_9H_{13}N$	136.1121	−0.7	10.1	1.76	AM-D5
	Methamphetamine (MA)		$C_{10}H_{15}N$	150.1277	−1.3	10.21	2.07	MA-D14
	3,4-Methylenedioxyamphetamine (MDA)		$C_{10}H_{13}NO_2$	180.1019	−2.2	10.01	1.64	MDA-D5
	3,4-Methylenedioxy-N-methylamphetamine (MDMA)		$C_{11}H_{15}NO_2$	194.1176	−1.0	10.14	2.28	MDMA-D5
	3,4-Methylenedioxy-N-ethylamphetamine (MDEA)		$C_{12}H_{17}NO_2$	208.1332	−1.4	10.22	2.77	MDEA-D6
Cocainics	Cocaine (CO)		$C_{17}H_{21}NO_4$	304.1543	0.3	8.85	2.30	CO-D3
	Benzoylecgonine (BE)		$C_{16}H_{19}NO_4$	290.1387	−2.1	3.15 9.54	−1.32	BE-D3
	Cocaethylene (CE)		$C_{18}H_{23}NO_4$	318.1700	−3.5	8.77	2.66	CO-D3
Cannabinoids	Δ-9-Tetrahydrocannabinol (THC)		$C_{21}H_{30}O_2$	315.2319	−3.8	10.6	6.97	THC-D3
	11-Nor-9-carboxy-Δ-9-tetrahydrocannabinol (THC-COOH)		$C_{21}H_{28}O_4$	345.2060	−0.3	4.21	6.36	THC-COOH-D3