



## Occurrence and removal of drugs of abuse in Wastewater Treatment Plants of Valencia (Spain)



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### ABSTRACT

The occurrence of 8 drugs of abuse and metabolites in the influent and effluent of the 3 Wastewater Treatment Plants (WWTP) that treat wastewater from Valencia was studied in 2011, 2012 and 2013. Target drugs except 6-monoacetylmorphine (6-ACMOR) were detected in 100% of the influents. The WWTPs eliminate cocaine (COC), amphetamine (AMP), methamphetamine (MAMP) and 11-nor-9-carboxy- $\Delta^9$ -tetrahydrocannabinol (THC-COOH). Benzoylcegonine (BECG) was also efficiently eliminated (93–98%), whereas 3,4-methylenedioxyamphetamine (MDMA) presented removal rates of 32–57% and ketamine (KET) was not eliminated. The most consumed illicit drugs, according to the estimated concentrations of each compound in the studied WWTPs, were cannabis and COC followed by KET, AMP, MAMP, MDMA and heroin. Environmental risk assessment was evaluated by calculating Risk Quotient (RQ). MDMA and KET could pose a medium risk and low risk, respectively, to the aquatic organisms. Although short-term environmental risk is not worrisome, long-term effects cannot be known exactly.

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### 1. Introduction

Illicit drugs monitoring in waters can be useful because environmentalists manage and track environmental hazard of these substances and epidemiologists evaluate their nature, magnitude and consumption patterns. Sewage epidemiology provides an important tool for estimating local consumption by investigating mass flows of unchanged parent drugs or their metabolites. This methodology was proposed by Daughton (2001) and implemented for first time by Zuccato et al. (2005). Nowadays, it is considered a suitable alternative to estimate objectively consumption in real time (EMCDDA, 2008) and numerous research groups estimate drug of abuse use at the community level in Europe (Van Nuijs et al., 2011a), Australia (Lai et al., 2013), Canada (Metcalf et al., 2010) and North America (Bartelt-Hunt et al., 2009; Jones-Lepp et al., 2004). Relevant examples of this approach in individual European cities have been reported in Belgium (Van Nuijs et al., 2011c, 2009a, b), Croatia (Terzic et al., 2010), France (Karolak et al., 2010; Nefau et al.,

2013), Ireland (Bones et al., 2007), Italy (Zuccato et al., 2008, 2005), The Netherlands (van der Aa et al., 2013), Spain (Bijlsma et al., 2014; Boleda et al., 2009; Huerta-Fontela et al., 2008; Postigo et al., 2010), Sweden (Östman et al., 2014), Switzerland (Zuccato et al., 2008) and United Kingdom (Kasprzyk-Hordern et al., 2009a). Currently numerous research groups, including our own, are carrying out an effort to homogenize these techniques to collective level, such as the study conducted in 19 European cities comprising Valencia (Thomas et al., 2012).

In this study, 8 compounds selected for their high traditional consumption in Spain, were analyzed for 3 consecutive years (periods from one week to one fortnight depending on the year) in influents and effluents from 3 Wastewater Treatment Plants (WWTPs) that treat most of the wastewater of Valencia and its surrounding towns, located in eastern Spain. The overall consumption levels for the drugs in the different collection periods were calculated as the mean of each WWTP, while the results from the daily samples were used to evaluate weekly variations. In addition, the removal efficiencies of the WWTPs and the elimination of target analytes were evaluated and the effects of the different wastewater treatments were ascertained. The impact of treated wastewater effluent on the quality of receiving waters was

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also investigated performing an ecotoxicological risk assessment. To achieve these objectives advanced mass spectrometry techniques such as ultra high pressure liquid chromatography triple quadrupole mass spectrometry (UHPLC-QqQ-MS/MS) and ultra high pressure liquid chromatography quadrupole time-of-flight (UHPLC-QqTOF-MS/MS) were used.

## 2. Experimental

### 2.1. Reagents and materials

High purity (>99%) standard solutions of 6-acetylmorphine (6-ACMOR), amphetamine (AMP), benzoylecgonine (BECG), cocaine (COC), ketamine (KET), methamphetamine (MAMP), 3,4-Methylenedioxymethamphetamine (MDMA), at 1000 mg L<sup>-1</sup> and 11-nor-9-carboxy-Δ<sup>9</sup>-tetrahydrocannabinol (THC-COOH) at 100 mg L<sup>-1</sup> in methanol were obtained from Cerilliant (Austin, TX, USA) and LGC GMBH (Luckenwalde, Germany). Working standard solutions of the analytes were prepared at different concentrations by appropriate dilution of the individual stock solutions in methanol-water (1:9, v/v). The deuterated drug analogs 6-ACMOR-d<sub>3</sub>, AMP-d<sub>5</sub>, BECG-d<sub>3</sub>, COC-d<sub>3</sub>, KET-d<sub>4</sub>, MAMP-d<sub>5</sub>, MDMA-d<sub>5</sub>, and THC-COOH-d<sub>3</sub> – used as internal standards (IS) – were also obtained from Cerilliant and LGC GMBH at a concentration of 100 mg L<sup>-1</sup> in methanol. A mixed ISs working solution at 1 mg L<sup>-1</sup> was prepared in methanol. Calibration standards were prepared by serial dilution of the mixed working solution ranging from 0.25 ng mL<sup>-1</sup> to 250 ng mL<sup>-1</sup> and addition of ISs working solution at constant concentration of 6.25 ng mL<sup>-1</sup>. These levels considering the concentration factor would be equivalent to 1–1000 ng L<sup>-1</sup> and 25 ng L<sup>-1</sup>, respectively, in the water samples. Stock and working solutions were stored at –20 °C in the dark.

Water used for preparation of calibration standards and UHPLC-MS/MS mobile phase was purified by an Elix Milli-Q system (Millipore, Billerica, MA, USA). Methanol was purchased from Panreac (Castellar del Vallès, Barcelona, Spain) and formic acid was from Amresco (Solon, OH, USA). Phenomenex (Torrance, CA, USA) Strata X SPE cartridges (500 mg/6 mL, surface area 800 m<sup>2</sup> g<sup>-1</sup>, particle size 33 μm, average pore size 85 Å) were used to extract analytes from water samples.

### 2.2. Sampling

Samples were collected from the influent and effluent of 3 different WWTPs in Valencia (Pinedo I, Pinedo II and Quart-Benàger), receiving wastewater from Valencia and other small surrounding towns. The catchment area of Pinedo I and Pinedo II consists of 351,000 and 943,000 inhabitants, respectively, while the catchment area of Quart-Benàger consists of 215,000 inhabitants. The main characteristics of each WWTP are summarized in Table 1. Sampling campaigns were carried out in 3 years, 2011 (March 9th to 15th), 2012 (April 17th to May 1st) and 2013 (March 6th to 12th).

Samples (24 h composite) were collected using the operational equipment of the WWTPs in a time-proportional manner at 60 min time intervals. Sampling strategies for wastewater were already examined by Ort et al. (2010) and evaluated by Castiglioni et al. (2013). Composite samples instead of grab samples were selected in this study to get the maximum representativeness. A daily grab sample would never be representative because the concentration of the analytes varies along the day. Although some compounds can be significantly degraded (>15%, after 12 h) in composite samples (Baker et al., 2012), the analytes selected in this study for back-calculations AMP, MAMP, BECG, KET and THCOOH are generally stable (Baker et al., 2012; Castiglioni et al., 2013). The sampling interval (60 min) was fixed by the WWTPs. According to Ort et al. (2010) and Castiglioni et al. (2013), considering population size, uncertainty is lower than 5% using this time interval.

All samples were stored in polyethylene terephthalate (PET) bottles. Once the samples arrived at the laboratory they were immediately frozen at –20 °C until analysis to prevent degradation of the illicit drugs.

### 2.3. UHPLC-MS/MS

#### 2.3.1. UHPLC-QqQ-MS/MS

Chromatographic separation was performed using an Agilent 1260 UHPLC (Agilent, Waldbronn, Germany). The separation was carried out with a Phenomenex Kinetex C18 (1.7 μm, 100 Å, 50 × 2.10 mm) at temperature of 30 °C and constant flow rate of 0.2 mL min<sup>-1</sup>. The mobile phase was eluent A (formic acid 0.1% in water) and eluent B (formic acid 0.1% in methanol). The gradient elution was started at 10% B maintained for 5 min, then increased linearly to 95% B in 12 min and remained constant at 95% B up to 25 min, then it returns to the initial conditions with an equilibrium time of 15 min. The injection volume was 5 μL. The injection was long to use a flow compatible with MS detection. The UHPLC was coupled to an Agilent 6410 triple quadrupole mass spectrometer with an electrospray ionization source working in the positive ionization (ESI<sup>+</sup>) mode, 300 °C gas temperature, 11 L min<sup>-1</sup> gas flow and 25 psi nebulizer. The optimal quantification and confirmation transitions as well as the specific MS parameters were optimized for each compound (Table S1).

#### 2.3.2. UHPLC-QqTOF-MS/MS

The chromatography was performed on an Agilent 1260 Infinity using the same conditions as in the previous section. The UHPLC system was coupled to a hybrid quadrupole time-of-flight ABSciex Triple TOF<sup>TM</sup> 5600 (Framingham, MA, USA). The MS acquisition was performed in positive ionization using information-dependent acquisition (IDA) that consist of two experiments: the survey scan type that was a full scan mass spectrum between *m/z* 100–950 and the information dependent scan that was product ion mass spectrum of the selected precursor: ion spray voltage, 5500 V; declustering potential (DP) 80 V; collision energy (CE) 10 V; temperature 450 °C with curtain gas (CUR) 30 (arbitrary units); ion source gas 1 (GS1) 35 and ion source gas 2 (GS2) 35. IDA MS/MS was performed using the following criteria: ions that exceeded 100 cps, ion tolerance 50 mDa, and collision energy fixed at 45 V.

**Table 1**

Description of the different WWTPs.

	Pinedo I	Pinedo II	Quart-Benàger
<b>Population served (hl)</b>	351,000	943,000	215,000
<b>Municipalities</b>	Valencia	Valencia and surrounding towns	Valencia and surrounding towns
<b>Treated wastewaters</b>	100% Urban	100% Urban	40% Urban/60% industrial
<b>Treated technology</b>			
Primary	Settlement/physicochemical	Settlement/physicochemical	Settlement/physicochemical
Secondary	Activated sludge	Denitrification by activated sludge	Activated sludge/phosphorous removal
Tertiary	Coagulation/flocculation/filtration	Coagulation/flocculation/filtration	Coagulation/flocculation
<b>Influent characteristics</b>			
Flow (m <sup>3</sup> /day)	117,211 ± 2633	244,817 ± 48,565	34,888 ± 4706
T °C	17.2	17.3	18.4
pH	7.7	7.6	7.8
BOD <sub>5</sub> (mg L <sup>-1</sup> )	223.1	264.2	367.1
COD (mg L <sup>-1</sup> )	396.3	473.4	625.4
N (mg L <sup>-1</sup> )	36.4	37.0	55.7
P (mg L <sup>-1</sup> )	4.9	4.7	7.3
NH <sub>4</sub> (mg L <sup>-1</sup> )	31.7	25.2	38.8
<b>Effluent characteristics<sup>a</sup></b>			
T °C	15.3	14.6	18.0
pH	7.6	7.4	7.5
BOD <sub>5</sub> (mg L <sup>-1</sup> )	9.7	2.4	5.0
COD (mg L <sup>-1</sup> )	40.8	15.8	30.6
N (mg L <sup>-1</sup> )	32.4	6.7	9.3
P (mg L <sup>-1</sup> )	2.4	0.3	0.7
NH <sub>4</sub> (mg L <sup>-1</sup> )	17.0	0.2	3.9

T: temperature; BOD<sub>5</sub>: biochemical oxygen demand; COD: chemical oxygen demand; N: nitrogen; P: phosphorus; NH<sub>4</sub>: ammonium.

<sup>a</sup> The effluent flow is the same as influent flow.

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