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Occurrence of drugs of abuse and benzodiazepines in river waters from the Madrid Region (Central Spain)

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HIGHLIGHTS

- Drugs of abuse detected in waters from two rivers in the Madrid Region.
- Concentrations measured are comparatively higher than in Europe.
- Ephedrine, benzoylecgonine, EDDP and lorazepam are the most abundant compounds.

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ABSTRACT

This work investigates, for the first time, the occurrence of 10 drugs of abuse, six metabolites, and three benzodiazepines in surface waters from the Jarama and Manzanares Rivers in the Madrid Region, the most densely populated area in Spain and one of the most densely populated in Europe. The results of this study have shown the presence of 14 out of the 19 compounds analyzed at concentrations ranging from 1.45 to 1020 ng L^{-1}. The most ubiquitous compounds, found in 100% of the samples, were the cocaine metabolite benzoylecgonine (BE), the amphetamine-like compound ephedrine (EPH), the opioids morphine (MOR), methadone (METH), and the METH metabolite 2-ethylene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), and the three investigated benzodiazepines alprazolam (ALP), diazepam (DIA) and lorazepam (LOR). Meanwhile, the largest concentrations observed corresponded to EPH (up to 1020 ng L^{-1}), BE (823 ng L^{-1}), EDDP (151 ng L^{-1}), and LOR (167 ng L^{-1}). The only not detected compounds were heroin (HER) and its metabolite 6-acetylmorphine (6ACM), lysergic acid diethylamide (LSD) and its metabolite 2-oxo-3-hydroxy-LSD (OH-LSD), and Δ^9-tetrahydrocannabinol (THC). Overall, the levels measured are comparatively higher than those previously reported in Europe. Comparison of the results obtained for samples collected on different days (Thursday and Sunday) did not show meaningful differences between weekdays and weekends. The lack of (eco)toxicological data does not permit to predict or disregard potential adverse effects on wildlife. Risk assessment in humans would require further knowledge, not currently available, on exposure to these compounds through other routes like drinking water and/or food.

1. Introduction

In the last 20 years, the interest on the so-called "emerging pollutants" (EPs) has increased. This category of pollutants includes very different substances with both industrial and domestic applications and varying potential harmful effects (e.g. endocrine disruption, carcinogenicity, etc.), and, among them, the group of drugs of abuse (DAs) and their metabolites.

Abbreviations: 6ACM, 6-acetylmorphine; ALP, alprazolam; AM, amphetamine; ATS, amphetamine-type stimulants; BE, benzoylecgonine; CE, cocaethylene; CO, cocaine; DAs, drugs of abuse; DIA, diazepam; EDDP, 2-ethylene-1,5-dimethyl-3,3-diphenylpyrrolidine; EPs, emerging pollutants; EPH, ephedrine; HER, heroin; IDA, information-dependent acquisition; LC, liquid chromatography; Ldet, limit of determination; LOD, limit of detection; LOQ, limit of quantification; LOR, lorazepam; LSD, lysergic acid diethylamide; MA, methamphetamine; MDMA, 3,4-methylenedioxymethamphetamine; METH, methadone; MOR, morphine; MR, Madrid Region, MS/MS, tandem mass spectrometry; MS, mass spectrometry; n.a., not available; n.c., not confirmed; n.d., not detected; OH-LSD, 2-oxo-3-hydroxy-LSD; RSP, river sampling point; SPE, solid phase extraction; SRM, selected reaction monitoring; STP, sewage treatment plant; THC, Δ^9-tetrahydrocannabinol; THC-COOH, 11-nor-9-carboxy-Δ^9-tetrahydrocannabinol; UNODC, United Nations Office on Drugs and Crime.

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The United Nations Office on Drugs and Crime (UNODC) has recently published its last World Drug Report (UNODC, 2012). Around 230 million people (5% of the world's adult population, aged from 15 to 64) are estimated to have used an illicit drug at least once in 2010. According to the same report, the extent of global illicit drug use remained stable in the five years up to and including 2010, at between 3.4% and 6.6% of the adult population. Cannabis is the world's most widely used illicit substance; in 2010, there were between 119 and 224 million cannabis users worldwide and consumption was stable (annual prevalence from 2.6% to 5%). The second most widely used class of drugs worldwide is the amphetamine-type stimulants (ATS), mainly methamphetamine (MA), amphetamine (AM) and "ecstasy" (3,4-methylenedioxymethamphetamine, MDMA). While the estimated use and global seizures of ATS remained largely stable, 2010 was marked by an increase in MA seizures to more than double the amount in 2008, partly due to seizures increasing in Central America and East and South-East Asia. There were, in 2010, between 14 and 53 million ATS users excluding "ecstasy" (annual prevalence from 0.3% to 1.2%) and between 10 and 28 million "ecstasy" users (annual prevalence from 0.2% to 0.6%). The opioids, with an estimated annual prevalence ranging from 0.6% to 0.8% of the adult population (between 26 and 36 million people), are the third one. Their use (mainly HER, MOR, and non-medical use of prescription opioids) is stable in all of the main markets. Finally, cocaine (CO) shows an estimated annual prevalence ranging from 0.3% to 0.4% (between 13 and 20 million people). LSD and other hallucinogenic substances were broadly popular in the 1960s; nowadays the use of hallucinogenic substances has not disappeared but it is now much less widespread.

The last Spanish survey about alcohol and drugs (EDADES, 2011/2012), in line with the above report and the annual report on the state of the drugs problem in Europe published by the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA, 2012), points out a general decrease or stabilization of drugs consumption with one exception, the family of sedatives, which includes benzodiazepines, consumed in the last year by 11.4% of the population.

In Spain cannabis is the most consumed substance although its consumption has decreased (prevalence of 10.6% in 2009 compared to 9.6% in 2011). Cocaine is the second one with a prevalence of 2.2%, following the descending trend started in 2007. It shows an alarming datum, 1.2% of young people, between 15 and 17 years old, reveal its consumption in the last year, placing Spain at the head of Europe in this age range. The descending trend, initiated in 2001, in the consumption of ecstasy (0.7%), amphetamines (0.6%), hallucinogenic (0.4%) and heroin (0.1%), becomes consolidated (EDADES, 2011/2012).

After these striking figures, the detection of these substances and/or their metabolites in the sewage system following consumption, and thereafter in the receiving aquatic environment, is not surprising. To this end, their illegal condition and/or abused use comes to aggravate the problem by preventing their adequate disposal and control of residues. This, jointly with the recent development of advanced analytical methods for their determination in water, has led to their detection in surface water and even in tap waters. The occurrence of DAs and benzodiazepines has been reported in different European surface waters from Italy (Calamari et al., 2003; Zuccato et al., 2005, 2008a), Ireland (Bones et al., 2007), Belgium (Gheorghe et al., 2008; van Nuijs et al., 2009a,b), Romania (Moldovan et al., 2007), Germany (Ternes, 2001), and UK (Kasprzyk-Hordern et al., 2008; Zuccato et al., 2008a). Some studies have been developed in North America (Bartelt-Hunt et al., 2009; Loganathan et al., 2009; Jones-Lepp et al., 2012). In Spain, the occurrence of DAs and benzodiazepines in surface waters has been evaluated in several areas, including, in the North-East, Catalonia (Boleda et al., 2007, 2009; Huerta-Fontela et al., 2007, 2008; Postigo et al., 2008a) and the Ebro River Basin (Gros et al., 2010; Postigo et al., 2010; Pedrouzo et al., 2011), in the East, L'Albufera National Park (Vázquez-Roig et al., 2010) and Natural Park of Pego-Oliva Marsh (Vázquez-Roig et al., 2012) both in Valencia, in the North-West, Galicia (Esteban et al., 2012), and finally in the centre of Spain, Madrid (González-Alonso et al., 2010; Martínez-Bueno et al., 2010, 2011; Valcárcel et al., 2011) and the Tagus River (Toledo province) (Valcárcel et al., 2012, 2013).

In this context, the main objective of the present study was to explore for the first time the occurrence of DAs, metabolites, and benzodiazepines in surface water samples from the Manzanares and Jarama Rivers on their way through the Madrid Region (MR, Central Spain), which is the most densely populated area in Spain and one of the most densely populated also in Europe. Additional purposes of the work were to investigate potential fluctuations in drug concentrations between weekdays and weekends, and eventual direct drug discharges to the sewage or river systems through evaluation of the CO/BE and METH/EDDP ratios.

2. Materials and methods

2.1. Description of the sampling site

The MR, with 809.49 inhabitants per km^2, is the most densely populated region of Spain. Its area, 8028 km^2 (1.6% of the Spanish territory), is occupied by an estimated population of 6 498 560 inhabitants. A total of 81.90% of the population is concentrated in a conurbation composed by the city of Madrid (49.75%) and the municipalities in the metropolitan area (32.15%) (INEbase, 2012).

Map showing the study area and the location of the sampling are shown in Fig. 1. Characteristics of the sampling points can be seen in Table 1. Seven sewage treatment plants (STPs) from the MR were selected based on the population served. River water samples were collected approximately 100 m downstream from the point of emission of each STP. These STPs discharge their effluents directly into two important rivers of the MR: Manzanares River (river sampling points RSP1, RSP5, RSP6 and RSP7) and Jarama River (RSP2, RSP3 and RSP4).

River water grab samples were collected on 19th February (Sunday) and on 15th March (Thursday) 2012 from 9 am to 5 pm. On both days, mornings were cold but sunny, with temperatures near 5 °C, and afternoons were much warmer, with temperatures near 20 °C. Samples were taken in both campaigns at approximately the same time following the sequence: RSP2, RSP3, RSP1, RSP7, RSP5, RSP6, and RSP4. The samples were collected into 1 L PET bottles, and the pH, conductivity and temperature were measured immediately after. Once collected and during shipment samples were kept frozen at −20 °C.

2.2. Target compounds

Up to nineteen DAs and metabolites belonging to six different chemical classes (cocainics, ATSs, opioids, lysergic compounds, cannabinoids, and benzodiazepines) were monitored in the collected waters. Table 2 shows the target analytes, their CAS numbers, some physicochemical characteristics and their limits of detection and determination.

2.3. Analytical method

Upon reception in the laboratory for analysis, samples were fortified with a solution containing deuterium labeled analogs of the studied compounds at the following concentrations: 50 ng L^{-1} for the compounds CO-d3, BE-d8, METH-d3, MOR-d3, THC-d3, THC-