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Drugs of abuse and benzodiazepines in the Madrid Region (Central Spain): Seasonal variation in river waters, occurrence in tap water and potential environmental and human risk

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ABSTRACT

This work analyzes the seasonal variation (winter and summer) of ten 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. The occurrence of these compounds in tap water in this region is also investigated and a preliminary human health risk characterization performed for those substances found in tap water. Finally, a screening level risk assessment that combines the measured environmental concentrations (MECs) with dose–response data to estimate Hazard Quotients (HQs) for the compounds studied is also presented.

The results of this study show the presence of fourteen out of the nineteen compounds analyzed in winter and twelve of them in summer. The most ubiquitous compounds, with a frequency of detection of 100% in both seasons, were the cocaine metabolite benzoylecgonine (BE), the amphetamine-type stimulant (ATS) ephedrine (EPH), the opioid methadone (METH), the METH metabolite 2-ethylene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), and the three benzodiazepines investigated, namely alprazolam (ALP), diazepam (DIA) and lorazepam (LOR). The highest concentrations observed corresponded to EPH (1020 ng L^{-1} in winter and 250 ng L^{-1} in summer). The only compounds not detected in both seasons were heroin (HER) and its metabolite 6-acetylmorphine (6ACM), lysergic acid diethylamide (LSD) and its metabolite 2-oxo-3-hydroxy-LSD (O-H-LSD), and Δ^9-tetrahydrocannabinol (THC). In terms of overall concentration, all sampling points presented higher concentrations in winter than in summer. Statistical analyses performed to gather evidence concerning occasional seasonal differences in the concentrations of individual substances between summer and winter showed statistically significantly higher concentrations ($p < 0.05$) of BE, EPH and the opioid morphine (MOR) in winter than in summer. Two out of the nineteen compounds studied, namely cocaine (CO) and EPH, were detected in tap water from one sampling point at concentrations of 1.61 and 0.29 ng L^{-1}, respectively. The preliminary human health risk characterization showed that no toxic effects could be expected at the detected concentration level in tap water.

Abbreviations: a, aerobic stabilization; 6ACM, 6-acetylmorphine; ADI, acceptable daily intake; AF, assessment factor; ALP, alprazolam; AM, amphetamine; ATS, amphetamine-type stimulant; BAS, biologic-activated sludge; BB, bacterial bed; BE, benzoylecgonine; bf, belt-filter-drying; CBD, cannabidiol; CBN, cannabinol; CE, cocaethylene; CO, cocaine; CSO, combined sewer overflows; d, anaerobic digestion; DAs, drugs of abuse; DIA, diazepam; DWSP, drinking water sampling point; DWTP, drinking water treatment plant; EC50, median effective concentration; ECOSAR, Ecological Structure Activity Relationships; EDDP, 2-ethylene-1,5-dimethyl-3,3-diphenylpyrrolidine; EDI, estimated daily intake; EFSA, European Food Safety Authority; EPs, emerging pollutants; EPH, ephedrine; ERA, environmental risk assessment; EU, European Union; HER, heroin; HQ, Hazard Quotient; INE, Spanish Statistics Institute; LC, liquid chromatography; Ldet, limit of determination; L(E)C50, median lethal (effective) concentration; LOD, limit of detection; LOQ, limit of quantification; LOR, lorazepam; LSD, lysergic acid diethylamide; MA, methamphetamine; MDMA, 3,4-methylenedioxymethamphetamine; MEC, measured environmental concentration; METH, methadone; MOR, morphine; MR, Madrid Region; MS/MS, tandem mass spectrometry; MS, mass spectrometry; MSSSI, Spanish Ministry for Health, Social Services and Equality; n.a., not available; n.c., not confirmed; n.d., not detected; NIA, no information available; NOEC, no observed effect concentration; OECD, Organisation for Economic Co-operation and Development; O-H-LSD, 2-oxo-3-hydroxy-LSD; PEC, predicted environmental concentration; PET, polyethylene terephthalate; PNEC, predicted no effect concentration; PQ, physical–chemical processes; (Q)SAR, quantitative structure–activity relationship; 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; TF, tertiary filtration; TUs, toxic units; UNODC, United Nations Office on Drugs and Crime; US EPA, United States Environmental Protection Agency.

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The screening level risk assessment showed that MOR, EDDP and the THC metabolite 11-nor-9-carboxy-Δ^9-tetrahydrocannabinol (THC-COOH) were present in at least one of the sampling sites in a concentration leading to a Hazard Quotient (HQ) value between 1.0 and 10.0, thus indicating some possible adverse effects. The cumulative HQ or Toxic units (TUs) calculated for each of the groups studied showed that opioids and cannabinoids were present at concentrations high enough to potentially generate some adverse effects on at least one sampling point.

1. Introduction

The presence of drugs of abuse (DAs) (and/or their metabolites) in the water cycle as a consequence of their widespread consumption and poor elimination in water treatment plants is an issue of recent concern (Postigo et al., 2011a). As a result of their continuous introduction into the aquatic environment, these substances are behaving in a pseudo-persistent manner (Daughton and Ruhoy, 2008) and currently represent a new class of environmental emerging pollutants (EPs) that require attention (Boles and Wells, 2010; Richardson, 2008).

A World Drug Report (UNODC, 2013) published recently by the United Nations Office on Drugs and Crime (UNODC) informed that, in 2011, between 167 and 315 million people aged 15–64 (between 3.6% and 6.9% of the world's adult population) were estimated to have used an illicit substance in the preceding year. According to the same report, the prevalence of illicit drug use and the number of drug users with dependence or drug use disorders have remained stable. Since 2009, the prevalence of use of cannabis, opioids and opiates has increased whereas the prevalence of use of cocaine, amphetamine-type stimulants and “ecstasy”-group substances appears to have followed a declining trend between 2009 and 2011. This report also shows that the misuse or non-medical use of tranquilizers and sedatives such as benzodiazepines and barbiturates remains high and, at times, higher than other illicit substances.

A similar trend has been observed in Spain. According to the last Spanish survey on alcohol and drugs (EDADES, 2011/2012), a general decrease or stabilization of drug consumption has been observed with one exception, namely the family of sedatives, including benzodiazepines, consumed in the last year by 11.4% of the population. Among illicit drugs, cannabis continues to be the most consumed substance, followed by cocaine.

Although new water treatment technology for the removal of pollutants is being developed (Boleda et al., 2011a; Oller et al., 2011), more work needs to be done to improve its efficiency. In this respect, recent studies have confirmed the occurrence of these pollutants in surface, waste and tap water (Baker and Kasprzyk-Hordern, 2013; Boleda et al., 2011b; Esteban et al., 2012; Huerta-Fontela et al., 2011; Hughes et al., 2013; Hummel et al., 2006; Jones et al., 2005; Mompelat et al., 2009; Ort et al., 2010; Pal et al., 2012; Postigo et al., 2011a; Thomas et al., 2012; Valcárcel et al., 2012, 2013) and further studies are required to determine their consequences in the environment.

In light of the known leisure use of these substances, a large number of studies have tried to study the potential fluctuations in drug concentrations between weekdays and weekends, during holiday periods and among seasons (Baker and Kasprzyk-Hordern, 2013; Berset et al., 2010; Bijlsma et al., 2009; Boleda et al., 2009; Gerrity et al., 2011; Huerta-Fontela et al., 2008a, 2008b; Jones-Lepp et al., 2012; Loganathan et al., 2009; Mari et al., 2009; Metcalfe et al., 2010; Postigo et al., 2011b; Terzic et al., 2010; Valcárcel et al., 2013; van Nuijs et al., 2009, 2011). However varying findings in terms of daily and seasonal variations have been found in these studies, being thus difficult to come to clear conclusions.

Based on the last Spanish survey on water supply and sanitation 70.5% of urban water consumed in Spain has a domestic use. This urban water is obtained from surface (65%), ground (30%) and sea water (5%). The average consumption of tap water in private residences in the Madrid Region (MR) (141 L person^{-1} day^{-1}) is similar to the average in Spain (142 L person^{-1} day^{-1}) although it is the third Region in the total volume consumption rank (13.8%) (INE, 2013). The results included in the last Spanish technical report about the quality of the drinking water in Spain showed that in 2011 the sanitary quality of the tap water was suitable in 99.3% of the carried out analyses (MSSSI, 2011). However, as concentrations of emerging pollutants like illicit drugs, their metabolites and benzodiazepines are not included in the mandatory analysis, the results obtained in the present study, analyzing the presence of this kind of compounds in tap water, coming from both reservoirs and drinking water treatment plants, in the MR are novel and can be of interest to the water authorities.

Although the presence of these pollutants in water is well known, none of these substances have been subjected to an environmental risk assessment (ERA). Data provided by an ERA link the calculation of predicted or measured environmental concentration (PEC or MEC) with toxicity data in order to evaluate which compounds are more likely to pose a risk for aquatic organisms (Cooper et al., 2008). Few studies have applied an ERA approach to this class of emerging pollutants (Gros et al., 2010), in part because no laboratory-based toxicological data of the necessary requirements are available for most of these compounds. In this study we present, for the first time, a screening-level data set of toxicity values, based on (quantitative) structure–activity relationship ((Q)SAR) models, for the purpose of performing a preliminary, Tier I, risk characterization. The use of (Q)SAR models is becoming an integral part of the early stages of risk assessment, especially with compounds for which no laboratory based toxicological data are available. Indeed, their use in these early stages is encouraged by the European Commission under REACH regulation (EU, 2003a).

In this context, the main objectives of the present study were (i) to analyze the seasonal variation (winter–summer) of nineteen drugs of abuse, metabolites and benzodiazepines in surface water samples from the Manzanares and Jarama Rivers, two of the most important rivers in the Madrid Region (MR, Central Spain), (ii) to assess the presence of all of these substances in tap water samples from the same region, (iii) to compile a screening-level data set of toxicity values based on (Q)SAR models for the compounds studied and (iv) to preliminary characterize the environmental risk of these substances to aquatic ecosystems.

2. Materials and methods

2.1. Description of the sampling site

The Madrid Region (MR) is situated in Central Spain. Its capital, Madrid, holds 49.75% of the total MR population, and the surrounding municipalities in the metropolitan area account for an additional 32.15%. These figures make it the most densely populated region of Spain, with a population density of 809.49 habitants per km^2. Its area, 8028 km^2 (1.6% of Spanish territory), is occupied by an estimated population of 6,498,560 inhabitants (INEbase, 2012).

Two main rivers flow through this area. The Jarama River rises in the Central System mountain range and is one of the most important tributaries of the Tajo River. With a length of 190 km, it is the longest river in the MR, crossing it from North to South in the Eastern area. The Manzanares River, with a length of 92 km, is a tributary of the Jarama River and flows across the entire MR, passing through the city of Madrid, with a population of 3,233,527 habitants (INEbase, 2012).