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Estimation of illicit drugs consumption by wastewater analysis in Paris area (France)

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ABSTRACT

Illicit drugs consumption is actually an important public health concern that needs to be well defined to be managed. A new method, expressed as sewage epidemiology has been proposed by Daughton and developed by Zuccato. This method involves estimating the consumption from the measurement of drug residues in sewage. Several studies have been carried out, leading to an assessment of drugs consumption in some European countries. This work, carried out in Paris area (France) brings new data to this assessment and allows a comparison of cocaine and MDMA consumptions with European estimations.

Four wastewater treatment plants (WWTPs) have been retained for the study, taking into account biological treatment, volume capacity, geographic location and social environment. Cocaine and its major metabolite benzoylecgonine (BZE), amphetamine, 3,4-methylenedioxymethamphetamine (MDMA) and buprenorphine were measured in raw water and WWTP effluent using HPLC–MS/MS after SPE extraction. Amphetamine was rarely detected. Cocaine and BZE were quantified at levels from 5 to 282 ng L^{-1} and 15 to 849 ng L^{-1}, respectively. MDMA and buprenorphine concentrations remained under 20 ng L^{-1}. Cocaine consumption was estimated from cocaine or BZE concentrations measured in raw water and the results showed significant difference in drug taking during week or weekend. The estimated doses observed in this study are lower than those reported for others countries, especially Spain and Italy. MDMA consumption was estimated at lower levels than cocaine.

1. Introduction

Illicit drug consumption and abuse is a great social and health problem that meets with the difficulty of realistic consumption estimations. Indeed, statistics deduced from data obtained from medical centres, police statistics or health and social organizations prove that consumption is increasing. According to the last European Monitoring Centre for Drugs and Drug Addiction annual report [1], respectively 22.5 and 4 millions people in Europe have consumed cannabis or cocaine during the last year. In France, the percentage of 15–34 years old people consuming cocaine increased from 0.5% in 2000 to 1.2% in 2005.

As with pharmaceuticals, illicit drugs and their metabolites are eliminated through urban wastewaters and have been recognized as emerging environmental contaminants. Several studies have been carried out to evaluate illicit drugs concentrations in sewage waters at the entry of wastewater treatment plants (WWTPs): cocaine levels varied from several hundreds ng L^{-1} in Italy [2], in Belgium [3,4] or in Spain [5] to some μg L^{-1} in Catalonia in Spain [5,6]. For example, Huerta-Fontela et al. [6] found a median level for cocaine of 0.2 μg L^{-1} in 42 WWTPs influents with a wide range between 0.004 and 4.7 μg L^{-1} (Table 1). For the same samples, BZE concentrations varied from 0.009 to 7.5 μg L^{-1} and amphetamine concentrations between 3 and 688 ng L^{-1}. In comparison, Kasprzyk-Hordern et al. [7] analysed raw water of two WWTPs in South Wales and found mean levels of amphetamine (1196 and 4310 ng L^{-1}), higher than those of cocaine (207 and 521 ng L^{-1}) and benzoylecgonine (1082 and 992 ng L^{-1}). However, Castiglioni et al. [2] found low levels of amphetamine in influents of a WWTP located in Milano but they did not detect it in influents of a WWTP located in Lugano (Switzerland).

Drugs residual concentrations are detected in WWTPs effluents leading to contamination of surface waters: Zuccato et al. [8] reported mean cocaine levels from 0.5 to 44 ng L^{-1} in Italian rivers, and BZE levels 3–5 times higher.

Moreover, it has been shown that these levels followed consumption variations during weekends or special events such as music festivals [9]. An increase of consumption is observed for cocaine, ecstasy and amphetamine on Saturday/Sunday [6,8]. However, Mari et al. [10] observed variations along a year without clear tendency of consumption period.

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Table 1
Reported values of illicit drugs measured in influent in WWTP of European countries. Results are expressed as range or mean ± S.D., in ng L^{-1}.

Country	Localization	Cocaine	BZE	MDMA	Amphetamine	Reference
Spain	42 WWTP North-East Barcelona	4–4700 861 ± 214 (n = 7)	9–7500 4226 ± 1143 (n = 7)	2–598 134 ± 30 (n = 7)	3–688 41 ± 9 (n = 7)	Huerta-Fontela et al. [6] Postigo et al. [5]
Belgium	30 WWTP 5 WWTP	9–693 22–457	37–2130 82–1898			Van Nuijs et al. [4] Gheorge et al. [3]
Italy	Milano Florence	421 ± 83 (n = 8) 26–90	1132 ± 197 (n = 8) 86–214	14 ± 14 (n = 8)	15 ± 11 (n = 8)	Castiglioni et al. [2] Mari et al. [10]
Switzerland	Lugano	218 ± 58 (n = 8)	547 ± 169 (n = 8)	14 ± 13 (n = 8)	<LOQ (n = 8)	Castiglioni et al. [2]
South Wales	WWTP1 WWTP2	21–1837 54–471	126–2114 187–3715		292–12020 255–3225	Kasprzyk-Horden et al. [7]

In a context of public health, it appears essential to improve the assessment of consumption, i.e. to identify the geographic areas and the periods most favorable to drug consumption or abuse. Indeed, illicit drug consumption is supposed to be related to professional or social conditions. More, the quantities consumed can be improved during some festive events. Thus, it should be useful to define more closely the relation between drug consumption and social conditions. This is especially important for social organizations that work in the risk prevention in particular to prevent the transmission of AIDS or hepatitis C. The French government helps associations which manage and maintain street automatic dispensers of sterile syringes kit in aid of the drug-addicts and these associations need better consumption indicators to improve the dispenser deployment inside the city.

An innovative method has been described by Daughton [11] and developed by Zuccato et al. [12,13] to estimate drug consumption from wastewater measurements. Indeed, the quantity of drug consumed can be deduced from the drug or metabolite(s) flows measured in raw WWTP influent weighted from pharmacokinetic data, i.e. percentage of drug eliminated in the parent form or percentage of a specific metabolite in the metabolic pathways. This new estimation tool from sample collection to back-calculation has been adopted by the EMCDDA [14] as a realistic method and studies have been done in Belgium [4], Italy [10] and United-Kingdom [7].

The aim of this work was to assess, for the first time in France, the consumption in the city of Paris and greater suburban area, of four illicit drugs: cocaine, amphetamine, 3,4-methylenedioxymethamphetamine (MDMA) and buprenorphine. Buprenorphine is used under medical control for the treatment of opioid dependence. However, this compound is also used in an illicit manner and this is the reason why we choose to add it to the list of studied illicit drugs. In our knowledge, buprenorphine has never been included in published studies on illicit drugs in wastewater. Different WWTPs were selected according to the characteristics of treatment technologies, the volume capacity and the social and economic environment of the connected area.

2. Materials and methods

2.1. Sampling strategy

Four WWTPs have been selected and their characteristics are summarized in Table 2 and their location in Fig. 1. The choice was based on the comparison of two types of biological treatments (biofilters and activated sludges) and comparison of urban sectors with one privileged and one low-income area.

Several campaigns (n = 3–8) were carried out either on weekdays or weekends and a weekly campaign was also conducted at the WWTP 2, with daily collection during 7 consecutive days. Samples were made by the WWTP staff and corresponded to 24 h flow-weighted composite influent or effluent samples taken from 8:00 h one day to 8:00 h the following day. This sampling is made each day for the monitoring of the WWTP and a sample corresponds to about 10 L. Volumes between 2 and 3 L were taken for our laboratory to allow the repetition of analytical measurements. They were collected in glass amber bottles and stored at 4 °C before analysis that was performed within 24 h.

2.2. Chemicals and materials

Cocaine, BZE, MDMA, amphetamine, buprenorphine, cocaine-d3, BZE-d3, buprenorphine-d4, MDMA-d5 and amphetamine-d5 were purchased from LGC standards (Molsheim, France). Methanol and acetonitrile of HPLC grade (Hipersolv Chromanorm), formic acid (Normapur) and ammonium formate (Normapur) were obtained from VWR (Fontenay-sous-Bois, France). Ultra-pure water was produced using successive Milli-RO osmosis filtration and Milli-Q Plus water purification system (Millipore SAS, Molsheim, France).

SPE Oasis HLB cartridges (500 mg) and Xbridge Phenyl 3.5 μm, 3 mm × 150 mm HPLC column were purchased from Waters (Guyancourt, France).

A Dionex HPLC system, with Ultimate 3000 pump and a WPS 3000 PL sampler (Dionex, Voisins le Bretonneux, France) was coupled to a triple quadrupole mass spectrometer Quattro Ultima equipped with MassLynx software (Waters, Guyancourt, France).

2.3. Analytical measurements

Samples were filtered on glass fibers filters (1 μm, GFB Whatman) before SPE extraction. Oasis cartridges were rinsed with 2 × 5 mL methanol followed by 2× 5 mL ultra-pure water. Isotopically labelled compounds were added to 250 mL of WWTP influent or 500 mL of effluent samples (625 μL of a methanolic solution at 80 μg L^{-1} cocaine-d3, 160 μg L^{-1} BZE-d3 and 20 μg L^{-1} amphetamine-d5, MDMA-d5 and buprenorphine-d4) to obtain concentrations in the final extract of 100 μg L^{-1} for cocaine-d3, 200 μg L^{-1} for BZE-d3 and 25 μg L^{-1} for amphetamine-d5, MDMA-d5, and buprenorphine-d4. Samples were percolated through the cartridge at a flow rate of 2 mL min^{-1}. SPE cartridges were then washed using 5 mL ultra-pure water and dried for 30 min. Analytes were eluted with 10 mL of methanol and, after evaporation to dryness under a gentle stream of nitrogen, extracts were reconstituted in 500 μL of methanol. Each sample was analysed three times including SPE extraction repetition in the aim to verify intra-run precision for each run.

Chromatographic separation was performed with a binary mobile phase (Acetonitrile/ammonium formate buffer, 10 mM, pH 4) at a flow rate of 0.4 mL min^{-1} and the following gradient elution: 0–6 min, 5% acetonitrile, 6–26 min, increase to 90% acetonitrile, 26–31 min, 90% acetonitrile, 31–36 min, decrease to 5% acetonitrile. A 5 μL volume was injected.

Mass spectrometry was performed with positive mode electrospray ionisation and the following conditions: capillary voltage, 4.5 kV; source temperature, 120 °C;

Table 2
Characteristics of the four wastewater treatment plants (WWTP) studied.

	Capacity (m^3/day)[a]	Biological treatment	Sewage collection area
WWTP 1	600 000 (3 670 000)	Activated sludge	Paris south suburb
WWTP 2	240 000 (1 000 000)	Biological filters	Paris city and west suburb
WWTP 3	30 000 (250 000)	Activated sludge	Privileged urban sector
WWTP 4	30 000 (100 000)	Activated sludge	Low-income area

[a] Numbers of equivalent inhabitants are indicated in brackets.