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Presence of illicit drugs and metabolites in influents and effluents of 25 sewage water treatment plants and map of drug consumption in France

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HIGHLIGHTS

- Complete study with weekday and weekend samplings in 25 STPs in France.
- Qualitative and quantitative differences in illicit drug consumption are observed.
- LLAS treatments seem more efficient than MLAS treatments and biofilters.
- Methadone and its metabolite EDDP appeared difficult to remove whatever the treatment.

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ABSTRACT

Consumption of illicit drugs is a new concern for water management that must be considered not only because of the social and public health aspects but also in an environmental context in relation with the contamination of surface waters. Indeed, sewage treatment plant (STP) effluents contain drug residues that have not been eliminated since STP treatments are not completely efficient in their removal.

We developed and validated an HPLC–MS/MS analytical method to assess the concentrations of 17 illicit drugs and metabolites in raw urban wastewaters: cocaine and its metabolites, amphetamine and amphetamine-likes (methamphetamine, MDMA, MDEA, MDA), opiates and opiate substitutes (methadone and buprenorphine), and THC-COOH cannabis metabolite.

This method has been applied to the analysis of influent and effluent samples from 25 STPs located in France all over the country. The results allowed evaluating the drug consumption in the areas connected to the STPs and the efficiency of the treatment technology implied.

We selected STPs according to their volume capacity, their treatment technologies (biofilters, activated sludges, MBR) and their geographical location.

In influents, the concentrations varied between 6 ng/L for EDDP (main metabolite of methadone) and 3050 ng/L for benzoylecgonine (cocaine metabolite). Consumption maps were drawn for cocaine, MDMA, opiates, cannabis and amphetamine-like compounds. Geographical significant differences were observed and highlighted the fact that drug consumption inside a country is not homogeneous. In parallel, comparisons between STP technology processes showed differences of efficiency. More, some compounds appear very resistant to STP processes leading to the contamination of receiving water.

1. Introduction

The increasing use of illicit drugs and the nonmedical use of prescription medications are a growing concern for public health authorities. According to data supplied by surveys on populations, some 230 million people worldwide use illicit drugs each year (UNODC, 2012). When consumption data for the different drugs are combined, the numbers of European citizens who have used an illicit drug during their life reach approximately a third of the population (EMCDDA, 2012). These estimations are calculated from population surveys, seizure data and mortality rates related to illicit drug use. Such data makes it possible to improve our understanding of the evolution of drug consumption to develop appropriate prevention and harm-reduction programs. These approaches are however limited by their biases, especially a lack of representativeness. Using them, it takes a long time to establish a complete overview of consumption and, generally, results are published several years after the surveys. Hence, it is difficult to obtain a true estimation of current consumption and to follow its evolution. Moreover, current assessment techniques are generally not deployed to a defined scale, thus limiting true information for a specified area inside a country.

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Over recent years studies have been conducted to detect and measure the presence of illicit drugs in wastewaters. Indeed, drugs and medication are consumed, metabolized and eliminated from the human body in urinary and fecal excretions and the excreted parent compounds and metabolites are detectable in sewage. Based on this observation, Daughton (2001) proposed analyzing illicit drug residues to estimate the global consumption of a community. Then, Zuccato et al. (2005) published a new calculation method called "sewage epidemiology" that appears to be efficient for obtaining local and real-time estimates of drug consumption. Since 2005, different authors worldwide have used this method: Belgium (Gheorghe et al., 2008; Van Nuijs et al., 2011b), Croatia (Terzic et al., 2010), France (Karolak et al., 2010), Germany (Hummel et al., 2006), Ireland (Bones et al., 2007), Italy (Castiglioni et al., 2006; Zuccato et al., 2005; Mari et al., 2009), UK (Kasprzyk-Hordern et al., 2010), Spain (Huerta-Fontela et al., 2008; Boleda et al., 2009; Postigo et al., 2009; Bijlsma et al., 2012; González-Mariño et al., 2010; Pedrouzo et al., 2011), Switzerland (Berset et al., 2010), United States (Jones-Lepp et al., 2004; Chiaia et al., 2008; Loganathan et al., 2009; Bartelt-Hunt et al., 2009), Canada (Metcalfe et al., 2010) and Australia (Irvine et al., 2011; Lai et al., 2011). Recently, a multisite study has been run to compare drug consumption in nineteen European cities (Thomas et al., 2012).

In this study, seventeen compounds have been analyzed in influents and effluents from 25 STPs located in metropolitan France and an overseas department. We estimated drug consumption using sewage epidemiology method in order to establish a map and evaluate geographical drug consumption variations in France. In addition, we compared influent and effluent concentrations of the compounds in the different STPs in relation with their treatment process.

The following compounds were analyzed: first, the cocaine group that contains cocaine and its metabolites, benzoylecgonine, ecgonine methyl ester, norcocaine and cocaethylene which is formed when cocaine and alcohol are consumed simultaneously. Then, we analyzed the group of synthetic stimulant drugs including amphetamine, methamphetamine, 3,4-methylene-dioxy-N-methylamphetamine, 3,4-methylenedioxyamphetamine and 3,4-methylenedioxy-N-ethylamphetamine. In the opiate group, we chose to analyze heroin and its metabolites 6-monoacetylmorphine and morphine even if the latter has therapeutic prescriptions. We also analyzed two opiate substitutes, buprenorphine and methadone with its main metabolite 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine. Finally, we analyzed the 11-nor-delta-9-hydroxytetrahydrocannabinol that corresponds to the main metabolite of cannabis.

2. Materials and methods

2.1. Chemicals and materials

Standard solutions of cocaine (COC), benzoylecgonine (BZE), norcocaine (NOR), ecgonine methyl ester (EME), cocaethylene (CET), morphine (MOR), 6-monoacetylmorphine (6-MAM), heroin (HER), 3,4-methylene-dioxy-N-methylamphetamine (MDMA), 3,4-methylenedioxyamphetamine (MDA), 3,4-methylenedioxy-N-ethylamphetamine (MDEA), methamphetamine (MET), amphetamine (AMP), methadone (METD), 2-ethylidène-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), buprenorphine (BUP), 11-nor-delta-9-hydroxytetrahydrocannabinol (THC-COOH), cocaine-d3, BZE-d3, EME-d3, CET-d8, MOR-d6, 6-MAM-d3, HER-d9, MDMA-d5, MDA-d5, MDEA-d5, MET-d5, AMP-d6, METD-d3, EDDP-d3, BUP-d4, THC-COOH-d3, in methanol (MeOH) or acetonitrile (ACN), were purchased from LGC Standards (Molsheim, France).

MeOH and ACN, HPLC grade (Hipersolv Chromanorm), formic acid (FA) (Normapur) and ammonium formate (AF) (Normapur) were purchased from VWR (Fontenay-sous-Bois, France). Ultra-pure water was produced using successive Milli-RO reverse-osmosis filtration and the Milli-Q Plus water purification system (Millipore SAS, Molsheim, France).

Solid Phase Extraction (SPE) cartridges Oasis HLB (500 mg/6 mL) and Xbridge Phenyl 3.5 mm, 3 mm × 150 mm HPLC column were purchased from Waters (Guyancourt, France).

Analysis was carried out with a Thermo Accela pump and Accela sampler coupled to a triple quadrupole mass spectrometer Quantum Access Max equipped with Xcalibur software (ThermoFisher Scientific, Courtaboeuf, France).

2.2. Sampling strategy

25 sewage treatment plants (STP) were selected in order to have representative capacities, French locations and types of treatment (Fig. 1). We classified the STPs in three capacity groups of equivalent inhabitants (EI): big with EI > 100,000 EI, medium with EI ranging from 30,000 to 100,000 EI and small with EI close to 10,000 EI. Selected STPs were spread across the French metropolitan territory. Characteristics of the selected STPs are summarized in Table 1.

We arbitrarily divided the French metropolitan territory into 4 parts, North West (NW), North East (NE), South West (SW) and South East (SE) with big, medium and small STPs in each (Fig. 1). Besides, one STP in Paris (PAR) and one STP in Réunion Island (REU), a French overseas territory in the Indian Ocean, were also investigated.

At least two samplings were made, one during weekdays and one during the weekend for all STPs except SW5 due to logistic problems.

Sampling was carried out using cooling autosamplers to obtain 24 h flow-weighted composite influent or effluent samples with a sampling frequency of at least 6 times per hour according to the local STP procedures. At the end of sampling, 2 L samples were collected in polypropylene bottles and sent to laboratory in a cool box intended to be used for 24 h shipments. Upon receipt, samples were filtered and extracted according to the following protocol and the extracts were stored at 4 °C before analysis.

2.3. Analytical methods

2.3.1. SPE extraction

Samples were filtered on glass fiber filters (1 mm, GF/B Whatman) before SPE extraction. Isotopically labeled compounds were added to 250 mL of WWTP influent or 500 mL of effluent samples (250 μL of a 200 μg/L methanolic solution of each deuterated compound). Cartridges were conditioned by following elution of 2 × 5 mL MeOH and 2 × 5 mL ultra-pure water. Samples were percolated at a flow rate of 2 mL/min. The SPE cartridges were then washed using 2 × 5 mL ultra-pure water and dried for 30 min. Analytes were eluted with 2 × 5 mL of MeOH and eluates were evaporated to dryness under a gentle stream of

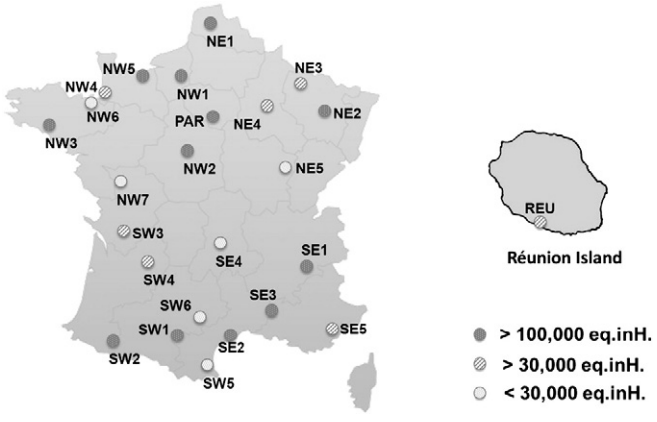

Fig. 1. Location of investigated STPs.