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National study of illicit drug use in Slovakia based on wastewater analysis

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HIGHLIGHTS

- We analyzed illicit drugs in wastewater of eight different Slovak cities.
- More than 20% of Slovak population were included in the study.
- High consumption of cheap drugs like methamphetamine was found.
- Two biggest Slovak music festivals affected local drug use different way.
- We revealed significant local differences in drug use pattern among the cities.

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ABSTRACT

The aim of this study was to analyze illicit drugs and their metabolites in wastewater from eight selected wastewater treatment plants (WWTPs) in Slovakia. The effect of two of the biggest music festivals in Slovakia on illicit drugs in wastewater was also investigated. Urinary bio-markers of amphetamine, methamphetamine, cocaine, cannabis and ecstasy use were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS). We then compared our results with data obtained in other parts of Europe and the world.

This study demonstrates that Slovakia has one of highest methamphetamine consumption rates in Europe. Within Slovakia, the highest level of methamphetamine consumption was found in Petržalka, where the mean specific load of this drug in sewage was 169 mg/day/1000 inhabitants; the next highest loads were detected in Piešťany (128 mg/day/1000 inhabitants) and Bratislava (124 mg/day/1000 inhabitants). Amphetamine, ecstasy and cannabis consumption in our study were comparable to that found in other European cities, whereas cocaine consumption was lower.

We also analyzed the pattern of drug consumption over the course of a week. The load of the cocaine metabolite benzoylecgonine in wastewater increased during the weekend. The use of this drug was most common in the capital of Slovakia. Increased consumption was also found during a folk festival in Piešťany. The ecstasy load in wastewater from larger cities also significantly increased over the weekend. An increase of drug consumption was also detected during a music festival in Trenčín, especially for ecstasy. The specific load of ecstasy during this festival increased from 3 mg/day/1000 inhabitants to 29 mg/day/1000 inhabitants. The possible influence of music styles on the consumption of certain drugs was also observed. During a folk festival, methamphetamine and cocaine were more commonly used.

1. Introduction

The drug situation in Europe is closely monitored by the European Monitoring Centre for Drugs and Drug Addiction and detailed in their annual report (EMCDDA, 2011, 2012). The 2012 report indicates that the number of Europeans undergoing treatment for drug addiction is constantly increasing. In 2011, 1.2 million Europeans were treated for drug addiction; 1609 individuals were treated in Slovakia.

Currently, the most commonly used drug in Western Europe is cocaine. Its use is particularly widespread in Denmark, Spain, the UK and Italy. Conversely, the use of amphetamine-type drugs prevails in northern European countries, such as Finland and Norway. Methamphetamine is the most commonly used drug in the Czech Republic

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and Slovakia. In Slovakia, methamphetamine production occurs mostly in small so-called "kitchen" laboratories (EMCDDA, 2011, 2012). Manufacturers of this drug use primarily over-the-counter (OTC) (non-prescription) medications containing the active ingredient ephedrine/pseudoephedrine (e.g., Modafen and Nurofen). Central European countries such as the Czech Republic and Slovakia can largely meet their own demand for methamphetamine.

In recent years, there has been an increase in the number of scientific studies focused on the incidence of antibiotics, pharmaceuticals, drugs and hormones in wastewater and subsequently, in the surface waters (Ort et al., accepted for publication; Repice et al., 2013; Thomas et al., 2012; Zhang et al., 2013; Zuccato et al., 2008; Zuccato and Castiglioni, 2009) resulting in wide-spread biological resistance to these types of compounds. Drug degradation in sewerage can be affected by many factors, such as the redox environment, sorption, sewerage length, physical and chemical mater of illicit drugs, temperature, season and wastewater pH, as well as the presence of some organic compounds (e.g., reduced sulfur compounds). Micropollutants such drugs and their metabolites can be partially biodegraded or sorbed in sewerage (Zeng et al., 2012; Zeng and Arnold, 2013). The effect of photodegradation on enclosed sewerage is minimal. In some cases, biological wastewater treatment is not sufficient to remove these substances from wastewater. Consequently, these drugs get into recipient water and can be cumulated, photodegraded and biodegraded (Zeng et al., 2012; Zeng and Arnold, 2013). This environmental micropollution can affect aquatic fauna and flora (Brodin et al., 2013).

Drug concentrations in wastewater usually range from a few units to hundreds of nanograms per liter (Irvine et al., 2011; Karolak et al., 2010; Metcalfe et al., 2010; Nefau et al., 2013). As in other countries or regions, the type of drugs and their concentrations in effluents can vary considerably depending on the region. In a study of 19 European cities, Thomas et al. (2012) demonstrated that the amount of illicit drugs used in an individual city can be determined with sufficient accuracy by wastewater analysis.

The aim of this study was to investigate illicit drug use in seven major Slovakian cities, including 20% of the Slovak population and representing geographical areas throughout Slovakia, using wastewater analysis. The analyses were performed from March through October 2013. Our study is the first to confirm data available from EMCDDA and indicates that methamphetamine is the most commonly used illicit drug in Slovakia.

2. Materials and methods

2.1. Standards and materials

LC–MS-grade methanol and acetonitrile (LiChrosolv, Hypergrade) were purchased from Merck (Darmstadt, Germany). Formic acid used to acidify the mobile phases was purchased from Labicom (Olomouc, Czech Republic). Ultrapure water for HPLC analysis was obtained from an Aqua-MAX-Ultrasystem (Younglin, Kyounggi-do, Korea).

Amphetamine, benzoylecgonine, cocaine, MDA, MDEA, MDMA, methamphetamine, methylphenidate, THC-COOH, amphetamine-D5, benzoylecgonine-D8, cocaine-D3, MDAD5, MDMA-D5, methamphetamine-D5, and THC-COOH-D9 were purchased from Cerilliant (Round Rock, Texas, USA) as 0.1 or 1 mg/L standards in either methanol or acetonitrile. All of the substances were classified as >99% pure. A spiking mixture was prepared by diluting stock solutions in methanol to a final concentration of 1 mg/mL for each compound and stored at −20 °C.

2.2. Sampling and analysis

The concentrations of illicit drugs in 24-hour composite samples from eight Slovak waste treatment plants (WWTPs) were determined. Raw wastewater was sampled from the influents of individual WWTPs, and the influent samples were collected using an automatic sampler device in 15-minute intervals over a 24-hour period beginning at 7:00 AM. The pooled samples were collected in plastic bottles and frozen at −20 °C within 2 h after the sampling. This procedure is consistent with the sampling protocol used by Thomas et al. (2012) to compare illicit drug consumption based on waste water analysis. The sewage samples were transported to the analytical laboratory and allowed to thaw at room temperature prior to the analysis. A mixture of isotope-labeled internal standards was added to 10 mL of homogenized and filtered (regenerated cellulose syringe filter, 0.45 μm pore size) water prior to analysis. The pooled water samples were analyzed in triplicate. The extraction and analysis were performed in a single step using on-line solid phrase extraction (SPE) liquid chromatography coupled with Q-Exactive, a hybrid quadrupole Orbitrap high resolution mass spectrometer (Thermo Scientific) (Fedorova et al., 2013). Isotope dilution and internal standard methods together with matrix-matched standards were used to eliminate matrix effects. The limit of quantification (LOQ) values calculated from the calibration curve and corrected for matrix effects were as follows: amphetamine: 5.8 ng/L, methamphetamine: 6.1 ng/L, benzoylecgonine: 4.6 ng/L, cocaine: 6.1 ng/L, MDMA: 9.4 ng/L, and THC-COOH: 2.0 ng/L. Triplicate relative standard deviation values were less than 10%, and in certain cases, under 30%. This method and its performance have been described in detail previously (Fedorova et al., 2013). The results were reported as the mean +/− the standard error.

2.3. Characterization of investigated locations

For the purpose of this study, seven large Slovak cities were selected as representatives of the urban population in the Slovak Republic (Fig. 1). The combined population of these cities is approximately 1.1 million, representing ca. 20% of the country's total population and more than one third of its urban population. Bratislava is a cosmopolitan capital and the most populated city in the Slovak Republic, with approximately 466,000 inhabitants. There are several colleges and universities in Bratislava with a combined total of approximately 60,000 students. It was estimated that during a working day, more than 150,000 people visit the city for work or entertainment. In 2009, there were 142 drug-related offenders per 100,000 inhabitants in Bratislava, which is significantly higher, than the national mean of 37 per 100,000 inhabitants. This higher drug-related offense rate may be due to the high population density of the city (Slovak police, 2013).

WWTP Bratislava includes wastewater not only from the city's center with its many foreign institutions, corporate offices of large companies, managers, artists and wealthy people but also from areas whose inhabitants are on the social periphery, poor sections of the city and suburbs known as drug centers, such as Pentagon (Slovak police, 2013; Statistical Office of the Slovak Republic). *Petržalka* is the largest suburb of Bratislava, with the highest population density in Slovakia as well as all of Central Europe. Previously known as the 'concrete jungle,' it is located next to the city center on the right bank of the Danube

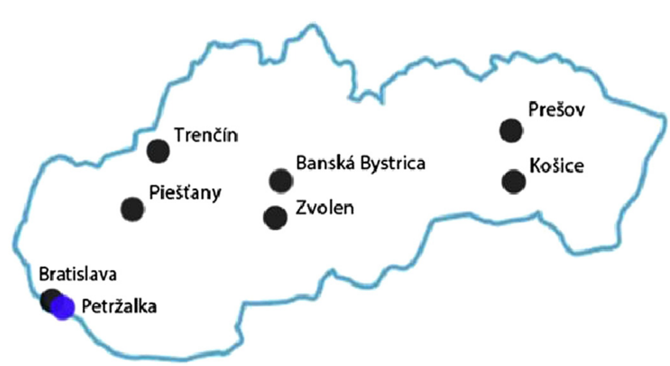

Fig. 1. Geographical map of Slovakia with the sampling sites.