

OCCURENCE OF LEGAL AND ILLICIT DRUGS IN WASTEWATER FROM DIFFERENT MUSIC FESTIVALS IN SLOVAK AND CZECH REPUBLIC AND POSSIBILITY OF THEIR EFFECTIVE DEGRADATION

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ABSTRACT

In our study, we have targeted on the presence of 12 drugs and metabolites in selected Slovak and Czech wastewater. Influent of five wastewater treatment plants were analyzed using LC-MS/MS. We have found out that among psychoactive compounds dominated methamphetamine in both countries. Subsequently, we have compared these obtained results with the prevalence of drugs in wastewater from 4 different music festivals (metal, dance, multi-genre and country). We have found increase of illegal drugs such as methamphetamine, cocaine and ecstasy in wastewater during festivals. We assume that this increase is connected with individual drug consumption, which may be linked to different musical styles. The highest increase of MDMA was detected during dance and multi-genre music festival. At metal and country festival the increase of methamphetamine was observed. Our results confirm the connection between dance music style preferences and cocaine and/or MDMA utilization.

In the last part of the study, we have focused on effective elimination of analyzed compounds directly from wastewater. Boron-doped diamond electrode, ferrates, Fenton reaction and its modifications have successfully degraded majority of investigated psychoactive agents under the detection limit.

Keywords: wastewater, music festivals, drugs, LC-MS/MS, degradation, Fenton reaction, ferrates, boron-doped diamond electrode

1. Introduction

Nowadays, the drug consumption in individual cities, regions, and at various music events and festivals in whole EU is usually monitored via questionnaires, medical data on treated patients, and from police interventions. This information is annually summarized by European Monitoring Centre for Drugs and Drug Addiction (EMCDDA, 2014). However, an overview on drug consumption obtained by these "methods" can be negatively affected by various factors. This way of the drug monitoring slowly respond to the occurrence of new drugs such as new types of stimulants. From this point of view, the determination of selected compounds in wastewaters significantly increases the accuracy of the data about legal and illicit drugs, and psychopharmaceuticals consumption (Mackul'ak *et al.*, 2014; Ort *et al.*, 2014).

1.1. Connection between drugs and music festivals

Several social studies also confirmed a connection between certain music preferences and drug utilization (De Alemida and Siva, 2005; Forsyth *et al.*, 1997). Main music genres such as dance,

rave, house or trance have been associated with increased frequency of ecstasy, speed, tobacco, alcohol, solvents, cannabis, inhalants, amyl nitrite, cocaine, LSD, benzodiazepines, ketamine, 'rave and hard drugs' and polydrug usage (De Alemida and Siva, 2005; Forsyth *et al.*, 1997). In 2011 Irvine published wastewater analysis study on the occurrence and consumption of drugs in the selected Australian cities (Irvine *et al.*, 2011). During this study the participants of music festivals were able to influence especially MDMA and cocaine prevalence in wastewaters. Mackuľak *et al.* (2014) monitored the drugs utilization during two large scale music festivals in Slovakia with more than 40.000 participants. During the multi genre music festival the increase of MDMA was observed. Contrary, cocaine was the main drug found during country festival (Mackuľak *et al.*, 2014).

1.2. Degradation drugs and pharmaceuticals compounds

Recently, the utilization of alga, enzymes, membrane reactors etc. is tested because the traditional wastewater treatment is usually not sufficient. The highest efficiency is achieved by AOPs (i.e. Fenton and Photo-Fenton reaction, ozonization, photolysis and their modification) utilization. Alternative ways of wastewater treatment – application of boron-doped electrodes or ferrates(VI) are also very effective (Feng *et al.*, 2013; Kotyza *et al.*, 2009; Li *et al.*, 2014).

Our study is focused on the monitoring of 12 drugs and their metabolites in sewages during music festivals. An increase of the concentration of almost all illicit drugs during festivals was detected in wastewater. Obtained results were compared with the drugs' load during non-festival days. In the second part of our study, the possibility of usage of the modified Fenton reaction, boron-doped electrodes, and ferrate(VI) for the degradation of illegal drugs was investigated. All of these ways are able to significantly decrease the drugs' concentration.

2. Materials and methods

2.1. Sampling and analysis

The concentrations of illicit drugs in 24-hour composite samples from two Slovak and two Czech waste water treatment plants (WWTPs) were determined (tab 1). 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 two hours after the sampling. This procedure is consistent with the sampling protocol used by Mackuľak *et al.* (2014) to compare illicit drug consumption based on wastewater analysis. LC-MS/MS method and its performance have been described in detail previously (Fedorova *et al.* 2013). The results were reported as the mean +/- the standard error.

2.2. Degradation techniques

Four different degradation techniques were used.

Fenton reaction and its modification are described in Mackuľak *et al.*, 2015.

Potassium ferrate was prepared as follows: The electrolysis was performed in an oil thermostat with a calibrated sensor, stainless steel box and PTFE opened crucible with a sample (KOH). The reference connection of the thermocouple was immersed in a Dewar flask with ice water. The measuring connection of the thermocouple was immersed in the melt at the same level as the electrodes. Anode was composed of mild steel class 11 (VALSTEEL, Czech Republic). Its minimum silicon content was 0.54 % (w/w), which was confirmed by SEM-EDS. The electrode consisted of five rods with a diameter of 8.5 mm and a height of 46 mm that were connected together. The counter electrode was composed of the same material as the anode. The cathodic and anodic compartments were divided by a diaphragm. The total volumes of the anodic and cathodic compartment were 80 mL and 130 mL, respectively. The mass fraction of KOH was less than 70 % (w/w). Based on the phase diagram, the temperature for this concentration was chosen to be 40 °C. The working anodic current density was optimized to be 20.3 mA.cm⁻². At the end of 25 hours of electrolysis, all of the anolyte was collected into a syringe and centrifuged for 30 minutes at 4000 rpm. Then, the potassium hydroxide solution was slowly poured out of the centrifuge test tube to separate the ferric compounds. After the

forced evaporation of the remaining solution, potassium ferrate in a stable solid form was obtained. The final concentration of the prepared potassium ferrate was approximately 80 % (w/w).

Heavily doped polycrystalline BDD film grown for 2 hours (1.3 μm thick) by double bias enhanced hot filament chemical vapor deposition (HF CVD) technique previously described [1, 2] was used as the electrode material. Highly conductive (0.008–0.024 Ohm.cm) N (100) type silicon wafer was used as the substrate for the BDD growth. Boron doping was achieved by adding trimethylboron (TMB) to the 2 % CH_4 in H_2 gas mixture with B/C ratio of 10 000 ppm. The total deposition pressure was 3 kPa and the substrate temperature $650\pm 20^\circ\text{C}$. The resistivity of BDD was 3.1×10^{-3} Ohm.cm and B concentration 4.7×10^{21} cm^{-3} , as measured by 4-point hall probe.

The electrochemical experiments were carried out in glassy beaker with 2 l of wastewater. All BDD electrodes used as anode were rectangular with active area of 5 cm^2 . Pt sheet with 1 cm^2 active area was used as cathode. Distance between the electrodes was set to 1 cm. A laboratory direct current power supply (GOLDSUN ELECTRONICS CO., LTD., GPS3005, Suzhou City, CHINA) provided a current density of 10 mA/cm^2 . During the electrolysis performed with continuous stirring at 500 rpm, the temperature of solution was kept at $22\pm 5^\circ\text{C}$.

2.3. Descriptions of the music festivals included in the study

Pohoda Festival is a multicultural festival that takes place near Trenčín. The average attendance is approximately 30 000 participants, making it the largest festival in Slovakia. During this festival, wastewater is removed through the sewerage to the Trenčín WWTP.

Grape Festival is a dance music festival organized at the Piešťany airport. In 2014, approximately 12 000 people attended the festival. The wastewater is completely processed at the WWTP Piešťany.

Gulaš fest, folk and country festival, is the largest Czech music festival, which takes place near Valašské Meziříčí. In 2014, approximately 20 000 people attended the festival. More than 70 % of wastewater is processed by the WWTP Valašské Meziříčí.

Small scale metal music festival Vandaalfest is organized nearby Zubří city. The number of participants is about 10 000. More than 90 % of wastewater is processed by the WWTP Zubří.

3. Results

In our work we have focused on the analysis of 12 drugs and metabolites (MDMA, methamphetamine, amphetamine, THC-COOH, caffeine, benzoylecgonine, heroin, 6-acetylmorphine, LSD, 2-Oxy-3-hydroxy-LSD (O-H-LSD), MDEA, MBDB) in wastewater during non-festival and festivals days (Valašské Meziříčí – Gulaš Fest, Zubří – Vandaalfest, Trenčín – Pohoda Fest and Piešťany – Grape Fest) using LC-MS/MS. Data were collected in June, July, and August 2014. The incidence of the compounds such as caffeine, heroin, 6-acetylmorphine, LSD, 2-Oxy-3-hydroxy-LSD (O-H-LSD), MDEA, and MBDB in wastewater was during festivals not significantly higher than during non-festival days. Therefore, these drugs were not more monitored.

Nowadays methamphetamine together with marihuana is the most widespread illegal drug in Slovakia and Czech Republic. The main reason is a simple and cheap production. Based on the EMCDDA statistics one can see the increase of methamphetamine utilization in both countries (EMCDDA, 2014). The dominance of methamphetamine in wastewater in the Czech Republic and Slovakia was confirmed (Tab. 1). This is in agreement with Golovko *et al.*, 2014 and Ort *et al.*, 2014 studies. The highest value of methamphetamine in wastewater was observed in Valašské Meziříčí and Zubří (446 ng/L and 339 ng/L). Although, the highest difference of methamphetamine load between festival and non-festival days was also recorded in these two cities, the increase of the drug concentration at all festivals was observed (Tab 1).

Based on these results one can conclude that the consumption of the specific drugs is connected with music style preference; e.g. during metal festival the increase of marihuana

secondary metabolite, amphetamine, and methamphetamine, during country festival amphetamine, and methamphetamine, during multi-genre (rock, pop, dance) festival marihuana secondary metabolite and MDMA, during dance festival MDMA and benzoylecgonine was observed (Tab 1).

Table 1: Concentration of selected drugs in wastewater during non-festival and festivals days

WWTP	Music style	Date	A	B	C	D	E
			ng/L				
Piešťany, SK	-	13 - 14.8.	25	242	<6	<6	34
Grape Fest	dance	15 - 16.8.	42	371	83	173	74
Trenčín, SK	-	14 - 15.7.	32	227	24	< 6	114
Pohoda Fest	multi	11 - 13.7.	38	253	38	138	260
Zubří, CZ	-	14 -15.8.	21	339	<5	<6	48
Vandaalfest Fest	metal	16 - 18.8.	46	560	9	<6	77
Valašské Meziříčí, CZ	-	21 - 22.7.	42	446	<7	<6	102
Guláš Fest	country	17 - 20.7.	80	776	<7	9	101

A – amphetamine; B – methamphetamine; C – benzoylecgonine; D - MDMA; E - THC-COOH; SK – WWTP in Slovakia, CZ – WWTP in Czech Republic

Compounds such as MDMA, methamphetamine or metabolite benzoylecgonine are only partially degraded at conventional WWTPs. Consequently, the undegraded compounds affect water ecosystem. The second part of the study was, therefore, focused on the remediation of illicit drugs and their metabolites in wastewater from the multi-genre music festival (12.7.2014). The ability for wastewater treatment of the Fenton reaction, modified Fenton reaction, BDDE, and ferrate were studied and results are listed in Tab. 2. All methods significantly decrease the concentration of the drugs in the sample. The highest efficiency was achieved in the case of FR and FLR. Both of these processes completely removed all analyzed micropollutants. Ferrate (efficiency 82%) and BDDE (efficiency 90%) were not able to decrease MDMA under the detection limit.

Table 2: Degradation of drugs and their metabolites during Pohoda Fest in wastewater from WWTP Trenčín (12.7.2014)

Drugs	WWTP Trenčín Pohoda Fest	FR	FLR	FE	BDDE
		ng/L			
amphetamine	39	< 5.1	< 5.4	< 6.2	< 4.9
methamphetamine	251	< 4.5	< 4.9	< 5.1	< 6.1
benzoylecgonine	66	< 2.8	< 2.9	< 3.2	< 3.0
MDMA	201	< 7.2	< 7.1	36	21
THC-COOH	412	< 2.3	< 2.1	< 3.1	< 2.7

FR – Fenton reaction; FLR – modified Fenton reaction; FE - ferrates, BDDE - boron doped diamond electrode

4. Conclusions

During music festivals, independently of music style, significant increase of biologically inert compounds such as MDMA, methamphetamine in wastewater was observed. The highest level was recorded in the case of MDMA at dance festival. During metal festival the increased concentration of amphetamine-like drugs was detected. The connection between music styles and the consumption of the different types of drugs was also found. Fenton and Fenton-like reaction, BDDE, and ferrate were used for wastewater treatment. Based on our results one can conclude that all of these processes significantly decrease drugs concentrations.

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