

OCCURRENCE OF AMPHETAMINES AND AMPHETAMINE-LIKE DRUG RESIDUES IN THE WASTEWATER TREATMENT PLANT OF THESSALONIKI (N. GREECE). ESTIMATION OF DRUGS' CONSUMPTION

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ABSTRACT

The consumption of illicit drugs in urban areas is a widespread and frequent phenomenon, especially during weekends and festivity days. Bioactive compounds and their metabolites are discharged through human excretion or direct disposal into domestic wastewaters (Zuccato et al., 2008). Sewage epidemiology is a novel approach aiming to assess illicit drugs' consumption based on the population of an area (Castiglioni et al., Willey ed.). A comprehensive study to develop and validate a method for the simultaneous detection and quantification of six (6) illicit drugs (amphetamines and amphetamines-like) was performed, including some of the most widely abused drugs (amphetamine, methamphetamine, 3,4-Methylenedioxyamphetamine (MDA), 3,4-Methylenedioxy-N-methylamphetamine (MDMA), 3,4-Methylenedioxy-N-ethylamphetamine (MDEA) and N-Methyl-1,3-benzodioxolylbutanamine (MBDB)). The developed method was implemented on samples from Thessaloniki's (Northern Greece) WWTP including influent and effluent.

The SPE method implemented used Oasis HLB cartridges, while chromatographic separation was achieved in an RP-C18 (1.7 μ m, 2.1 x 100mm) column, using a gradient program with water with 0.1% FA : MeOH with 0.1% FA. Detection and quantification of the compounds and their metabolites was realized using a Waters Acquity TQD LC-MS/MS (ESI+) system.

Relative recoveries reached 132%, while the method showed good repeatability and reproducibility. The limits of detection (LOD) of the method ranged 1.5 - 8.1 ng L⁻¹ and the limits of quantification (LOQ) ranged 5.1 - 24.6 ng L⁻¹.

The study revealed the daily presence of MDEA (6.7-14.3 ng L⁻¹) in the influent samples of WWTP. Also, MDMA was found only once (48.2 ng L⁻¹), on the sample of the 16/3 (Sunday). The presence of MDMA was justified because as a recreational drug it is expected to be found on a weekend, when the illicit drug consumption is more frequent. None of the analytes were detected in the effluent. Back calculation estimates that the daily consumption of MDEA is between 7 and 16mg/d/1000inh and for the day that MDMA was detected, the consumption was estimated to be 15mg/d/1000inh.

Keywords: amphetamines, illicit drugs, wastewater, drug epidemiology, back calculation, SPE, LC-MS/MS

1. Introduction

Consumption of illicit drugs is a widespread phenomenon, especially during weekends and holidays mainly in urban areas. Bioactive compounds and their metabolites are discharged through human excretion or direct disposal into domestic wastewaters (Zuccato et al., 2008). Drugs of abuse can also be persistent compounds and only partially are they decomposed through wastewater treatment. As a result drugs of abuse can potentially be detected in the treated water. Toxicity of illicit drugs on various organisms has not yet been studied. However, several studies have shown different toxicity levels on various organisms. Sewage epidemiology

is a novel approach aiming to assess illicit drugs' consumption based on the population of an area (Castiglioni et al., 2011).

2. Materials and methods

An analytical method for the determination of amphetamine, methamphetamine, 3,4-Methylenedioxyamphetamine (MDA), 3,4-Methylenedioxy-N-methylamphetamine (MDMA), 3,4-Methylenedioxy-N-ethylamphetamine (MDEA) and N-Methyl-1,3-benzodioxolylbutanamine (MBDB) was developed and validated during this study. The developed method was implemented on samples from Thessaloniki's (Northern Greece) WWTP including influent and effluent.

24 hour samples of wastewater influent and effluent were collected daily for 7 consecutive days from the WWTP of Thessaloniki. Chromatographic separation was achieved in an RP-C18 (1.7 μ m, 2.1 x 100mm) column, using a gradient program with water with 0.1% FA : MeOH with 0.1% FA. SPE utilized Oasis HLB (200mg, 6cc, Waters) cartridges. 200mL of each sample were used and eluted sequentially with acidic methanol solution and basic water solution. Selected compounds were identified and quantified using a Waters Acquity TQD LC-MS/MS. Positive ESI ionization in MRM mode was used, resulting in analysis time of 11 min. Two fragment ions were selected for the quantitative and qualitative determination of each compound.

3. Results and discussion

Chromatographic separation of the compounds was efficient with acceptable resolution values in 11 minutes. An assessment of various SPE cartridges led to the selection of the Oasis HLB (200mg, 6cc, Waters) cartridges for the needs of this study.

Analyte recoveries for most of the analytes ranged 65 - 132%, while the method showed good repeatability (2.2-5.4%) and reproducibility (2.5-5.8%). Analyte losses and matrix effects were compensated using MDEA as a surrogate standard and by using matrix matched calibration curves. The limits of detection (LOD) of the method ranged 1.5 - 8.1 ng L⁻¹ and the limits of quantification (LOQ) ranged 5.1 - 24.6 ng L⁻¹.

Analysis of wastewater samples originating from influents and effluents of WWTP of Thessaloniki during spring 2014, revealed the presence of MDEA (6.7-14.3 ng L⁻¹) on a daily basis in the influent samples. MDMA was also detected (48.2 ng L⁻¹), on one of the samples during the weekend. As a recreational drug MDMA is expected to be found on a weekend sample, when the illicit drug consumption is increased. None of the analytes were detected in the effluent.

An assessment of the daily consumption for these compounds can be carried out using back calculation estimates. In the case of MDEA this is between 7 and 16mg/d/1000inhabitants and for MDMA, the consumption was estimated to be 15mg/d/1000inh.

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