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Monitoring temporal changes in use of two cathinones in a large urban catchment in Queensland, Australia

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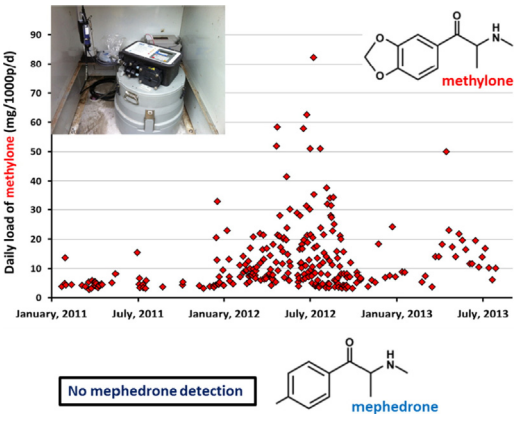
HIGHLIGHTS

- The first long-term regular monitoring of cathinones in wastewater
- The first application of direct injection LC/MS/MS for cathinones
- High detection frequency for methylone (45%) but no detection for mephedrone
- The data of methylone in wastewater matched well with other indicators.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater analysis was used to examine prevalence and temporal trends in the use of two cathinones, methylone and mephedrone, in an urban population (>200,000 people) in South East Queensland, Australia. Wastewater samples were collected from the inlet of the sewage treatment plant that serviced the catchment from 2011 to 2013. Liquid chromatography coupled with tandem mass spectrometry was used to measure mephedrone and methylone in wastewater sample using direct injection mode. Mephedrone was not detected in any samples while methylone was detected in 45% of the samples. Daily mass loads of methylone were normalized to the population and used to evaluate methylone use in the catchment. Methylone mass loads peaked in 2012 but there was no clear temporal trend over the monitoring period. The prevalence of methylone use in the catchment was associated with the use of MDMA, the more popular analogue of methylone, as indicated by other complementary sources. Methylone use was stable in the study catchment during the monitoring period

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whereas mephedrone use has been declining after its peak in 2010. More research is needed on the pharmacokinetics of emerging illicit drugs to improve the applicability of wastewater analysis in monitoring their use in the population.

1. Introduction

'New psychoactive substances' (NPS) is a term that refers to an expanding class of substances that often fall outside of domestic and international legal regulatory schemes (e.g. the 1961 United Nations Single Convention on Narcotic Drugs), but which may produce similar psychoactive effects to traditional scheduled substances and pose a threat to public health (Intergovernmental-Committee-on-Drugs, 2014; King and Kicman, 2011). Among them, synthetic cathinones such as mephedrone, pentedrone and MDPV (3,4-methylenedioxypyrovalerone) have become established in the illicit drug market internationally. In both European countries and in North America, cathinone use has been identified, particularly among consumers of other stimulant substances such as amphetamine and MDMA (or ecstasy) (EMCDDA, 2015; Underwood, 2015). In Australia, cathinone-based NPS are now a feature of the recreational drug market but little is known about the prevalence of use and the relationship between the NPS and ecstasy markets (Burns et al., 2014). Analyses of blood samples from fatally injured drivers suggest low rates of use of these NPS in the general population (Yap and Drummer, in press) and surveys suggest limited use of NPS among regular ecstasy users (Bruno et al., 2012). The most recent Australian Ecstasy and Related Drug Reporting System (EDRS) found that more than one-third of frequent ecstasy users reported that they had used NPS in the preceding six months, with the reported ratio in Queensland of >50% (Sindicich and Burns, 2015). However, the diversity of NPS available in the market and a lack of knowledge of the composition of substances purchased in illicit markets make it unclear to the user which NPS are being consumed.

Wastewater analysis, or wastewater-based epidemiology, is an objective, alternative method of monitoring population drug use. It involves measuring drug residues, excreted by drug users, in raw wastewater. The approach has become an important tool to estimate illicit drug use worldwide (Castiglioni et al., 2014) and has been intensively applied in Europe to estimate the consumption of illicit drugs such as cocaine, amphetamines, ecstasy, and cannabis (Ort et al., 2014). The availability of suitable analytical techniques and pharmacokinetic data has made estimating the use of these conventional drugs comparatively easy albeit some uncertainties related to wastewater analysis (Castiglioni et al., 2013). However, it remains a significant challenge to assess community use of NPS. The short history of these new substances means that their pharmacokinetics and their long-term adverse effects on human health are not well known. Furthermore, the status of NPS as illegal drugs in some jurisdictions makes it difficult to conduct research to understand the human pharmacokinetics of those compounds (Nutt, 2015).

The major drug reports in Australia that provide information on the self-reported use of NPS are the Ecstasy and Related Drug Reporting System (EDRS) and the Illicit Drug Data Report (IDDR); both are compiled annually (ACC, 2015; Sindicich and Burns, 2015). The EDRS is based on in-person interviews with regular drug users, key experts working in the drug and alcohol area who have regular contact with users, and the collation of indicators relating to drug use. The IDDR (produced by the Australian Crime Commission) reports data from across Australia on drug-related arrests and seizures as well as drug purity. Wastewater analysis and surveys are complementary because the former provides data on total community consumption of drugs while the latter provides detailed information on the behaviour of individual drug users.

In Australia, two of the most popular cathinones, mephedrone and methylone (German et al., 2014) have been reported in the EDRS survey since 2010 (for mephedrone and then since 2012 for methylone) (Bruno et al., 2012) and in analysis of wastewater (Chen et al., 2013; Lai et al., 2013). Both chemicals were scheduled as controlled substances in Queensland in September 2011 but no wastewater analysis study has evaluated the effectiveness of such regulation. Both these substances remain available to Australians through Dark Web marketplaces (Van Buskirk et al., 2015).

In this study we monitored temporal consumption trends in mephedrone and methylone (bk-MDMA) using wastewater analysis from a relatively large population in Queensland, Australia in three consecutive years (2011–2013). We then compared these data with those of a closely related drug, MDMA, in the same area. We also related these findings to data from the other official sources of information such as the EDRS and the seizure data. The rationale for this comparison was that MDMA and methylone are structurally similar (Fig. 1) and produce subjectively similar effects (Barceloux, 2012), and methylone is often found in pills sold as 'ecstasy' (i.e. as a substitute for MDMA).

2. Materials and methods

2.1. Wastewater sampling

The sampling setup has been described previously (Lai et al., 2015). Briefly, the sampling system was installed at the inlet of a wastewater treatment plant that served an urban catchment in South East Queensland (Australia) with a population of >200,000 people. Samples were collected between February 2011 and August 2013. From February 2011 to October 2012, samples were taken daily with some periods of break in between. From November 2012 to August 2013, sampling was scaled down to once a week on Tuesday or Wednesday due to limited access to the treatment plant during plant upgrades.

A continuous flow-proportional sampling technique was applied to ensure collection of representative daily composite samples from 6 AM to 6 AM next day (Ort et al., 2010). The samples were refrigerated at 4 °C during collection, acidified on site to pH 2 using 2 M hydrochloric acid and then frozen until analysis. Data on daily wastewater volumes were recorded by the WWTP.

2.2. Analysis of targeted compounds

Samples were analysed for the targeted compounds, mephedrone and methylone, using liquid chromatography (Shimadzu, Nexera UHPLC system, Kyoto, Japan) coupled with tandem mass spectrometry (AB SCIEX QTRAP® 5500, Ontario, Canada). The analytical method applied in this study was a combination of validated methods described previously (Lai et al., 2013, 2015). Briefly, an electronic robot (Tecan Genesis Workstation 200, Australia) was used to transfer filtered (Phenomenex 0.45 μm regenerated cellulose filters) samples into a vial that was then spiked with mixtures of deuterium-labelled internal standards (Mephedrone-D3 and Methylone-D3) at the level of 1 μg/L (1 ppb) to compensate for potential instrumental variability and matrix effects during analysis. Separation of the targeted analytes was performed on a Luna C18 (150 × 3 mm × 3 μm) analytical column (Phenomenex, Torrance, CA, USA). The mobile phases were solvent A (1% acetonitrile, 99% Milli-Q water and 0.1% formic acid) and B (95% acetonitrile, 5% Milli-Q water and 0.1% formic acid) with the optimized binary gradient: started at 8% B; ramped up to 35% B at 3.5 min; increased to 100% B at 7 min; held 100% B for 4 min; declined to 8% B and equilibrated the column for 3 min. Calibration standards were