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Occurrence of new psychoactive substances in wastewater of major Chinese cities

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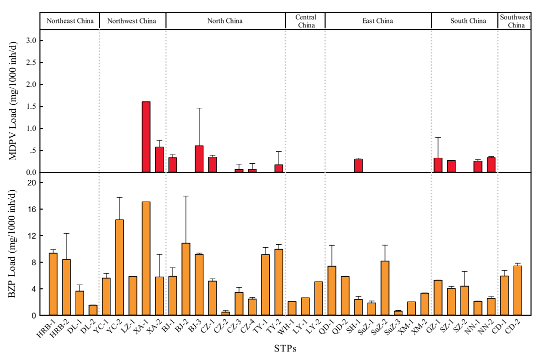
HIGHLIGHTS

- First nationwide reconnaissance on occurrence of NPS in wastewater in China
- Mephedrone, TFMPP, mCPP not detected wastewater across China
- MDPV detected at about 40% of the sampled cities with low concentrations
- BZP quantified in all the wastewater samples but showed no geographic pattern
- Apparent removal of MDPV was low, whereas removal of BZP was nearly complete.

GRAPHICAL ABSTRACT



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ABSTRACT

New psychoactive substances have become increasingly popular across the globe in recent years, which may cause certain public health issues. In this work, sewage-based epidemiology was applied to examine the use of two synthetic cathinones, mephedrone and methylenedioxypyrovalerone (MDPV), and three piperazines, benzylpiperazine (BZP), trifluoromethylphenylpiperazine (TFMPP), and 1-(3-Chlorophenyl)piperazine (mCPP), across China. Influent wastewater samples were collected from 36 sewage treatment plants (STPs) in 18 major cities that cover all the geographic regions of the country. Effluent samples were also collected from selected STPs to determine removal rates. Mephedrone, TFMPP, and mCPP were below detection limits in all the wastewater samples collected, indicating negligible use of these substances in China. MDPV was detected in wastewater at 13 STPs. However, its loads were <1 mg/1000 inh/d at most of these STPs, indicating low use of this substance. BZP was detected at all the STPs examined, with loads typically falling within the range of 3–10 mg/1000 inh/d. No clear geographic pattern in BZP occurrence in wastewater was identified. Since BZP in wastewater may also come from its legal sources, whether widespread occurrence of BZP means widespread abuse is yet to be confirmed. Apparent removal of MDPV by wastewater treatment was low (<25%), whereas removal of BZP was nearly complete (typically > 95%).

1. Introduction

New psychoactive substances (NPS) are substances that are not scheduled under the Single Convention on Narcotic Drugs of 1961 or the Convention on Psychotropic Substances of 1971, but it may pose a

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health threat comparable to that posed by substances listed in those conventions (UNODC, 2013). These substances are produced by slightly modifying the functional groups of the molecules of controlled drugs (e.g., cocaine, amphetamines). They have similar psychoactive effects of traditional drugs but can circumvent law enforcement. In the past few years, a fast growing number of NPS have been sold on illicit drug market. By December 2014, emergence of 541 NPS was reported by 95 member states and territories to United Nations Office of Drug and Crime (UNODC) (UNODC, 2015). In contrast, only 126 NPS were reported in 2009 (UNODC, 2013).

Given the widespread appearance of NPS on illicit drug markets, monitoring its abuse is warranted. However, even monitoring abuse of common illicit drugs is not an easy undertaking, as traditional monitoring methods, such as consumer interviews, medical records, crime statistics, and population survey are time-consuming and involve significant biases (Zuccato et al., 2008). Monitoring NPS abuse is much more challenging as consumption of these substances is so transitory and dynamic (Kinyua et al., 2015).

In the past decade, sewage-based epidemiology (SBE) has emerged as an effective tool to estimate drug prevalence and consumption within a particular population. This approach involves collecting wastewater samples, measuring the concentrations of drug residues or its metabolites, and back-calculating drug loads and consumptions by taking account of wastewater flow rates, community populations, as well as correction factors that account for excretion rates and stabilities of the drugs (Zuccato et al., 2008). It uses objective and quantifiable measures (i.e., drug residue concentrations, wastewater flow rates) and yields reliable and reproducible results. In addition, these results can be obtained in near real time as sample collection and analysis can be completed quickly. Thus this approach is particularly suitable to monitor the dynamic appearance and abuse of NPS.

Since its first application by Zuccato et al. in 2004 (Zuccato et al., 2005), SBE has been used to monitor use of traditional illicit drugs in many countries in Europe (Andres-Costa et al., 2014; Baker et al., 2014; Berset et al., 2010; Bramness et al., 2015; Kankaanpää et al., 2014; Karolak et al., 2010; Mackulak et al., 2014; Östman et al., 2014; Repice et al., 2013; van Nuijs et al., 2009), North America (Banta-Green et al., 2009; Bartelt-Hunt et al., 2009; Bisceglia et al., 2010; Brewer et al., 2012; Heuett et al., 2015; Loganathan et al., 2009; Metcalfe et al., 2010; Yargeau et al., 2014), East Asia (Du et al., 2015; Khan et al., 2014; Kim et al., 2015; Lai et al., 2013a; Li et al., 2014), and Australia (Irvine et al., 2011; Lai et al., 2015). Recently, a number of studies have also been performed in Europe and Australia to monitoring NPS abuse using the SBE approach (Baker and Kasprzyk-Hordern, 2011; Borova et al., 2015; Castiglioni et al., 2015; Chen et al., 2013; Kankaanpää et al., 2014; Kinyua et al., 2015; Mwenesongole et al., 2013; Reid et al., 2014; Thai et al., 2016; van Nuijs et al., 2014). Typically, NPS were detected at low concentrations or even below detection limits in those previous studies (e.g., Kinyua et al., 2015; Borova et al., 2015). The loads of detected NPS were much lower than those of primary drug of abuse (e.g., cocaine, MDMA, amphetamine). For example, the highest MDPV loads found in Finland was 19 mg/day/1000 inhabitants, whereas amphetamine loads in Finnish cities were >100 mg/day/1000 inhabitants (Kankaanpää et al., 2014). The average load of methylone was about four times lower than the average daily load of MDMA in an urban catchment in South East Queensland of Australia (Thai et al., 2016). Since target NPS monitored in these studies varied, systematic comparison of abuse of a particular NPS among different studies was not possible. In addition, removal rates and removal pathways of NPS during wastewater treatment have been rarely examined in the above studies.

China has witnessed rapid increases in illicit drug use in the recent years. The number of registered drug users increased by 20% from about 2.5 million of 2013 to nearly 3 million of 2014 (Office of China National Narcotic Control Commission, 2014, 2015). The total seizure of common illicit drugs (heroin, cannabis and cannabis resin, methamphetamine-like drugs, ketamine) has also increased by about 20%, from 42.26 ton of 2013 to 50.4 ton of 2014 (Office of China National Narcotic Control Commission, 2014, 2015). New psychoactive substances (e.g., cathinones, piperazines) are also seized in China from time to time, accordingly to the Bureau of Narcotics Control of the Ministry of Public Security (personal communication). It is worth noting that ketamine is categorized by UNODC as a NPS. However this drug has been widely abused in China and its seizure was second only to methamphetamine seizure in the past few years (Office of China National Narcotic Control Commission, 2014, 2015). Thus ketamine is really "not new" at all in China.

To date, four SBE studies has been performed in Hong Kong and mainland China to estimate common drug use (Du et al., 2015; Khan et al., 2014; Lai et al., 2013a; Li et al., 2014). However, none of these studies examined concentrations of cathinones and piperazines in wastewater in China. The objective of this work was to examine the occurrence and geographic pattern of two synthetic cathinones, mephedrone and MDPV, and three piperazines, BZP, TFMPP, and mCPP, in wastewater across China. Influent wastewater samples were collected from 36 STPs of 18 major cities that cover all the geographic regions of the country. Effluent samples were also collected from selected STPs to determine removal rates. This study represents the first nationwide reconnaissance dedicated specifically to NPS abuse in China.

2. Materials and methods

2.1. Sample collection

Wastewater samples were collected from 18 major cities that cover all the seven geographic regions of China: Haerbin (HRB) and Dalian (DL) of Northeast; Lanzhou (LZ), Xi-an (XA), and Yinchuan (YC) of Northwest, Beijing (BJ), Changzhi (CZ), and Taiyuan (TY) of North, Luoyang (LY) and Wuhan (WH) of Central China; Shanghai (SH), Qingdao (QD), Xiamen (XM), and Suzhou (SuZ) of East, Guangzhou (GZ), Nanning (NN), and Shenzhen (SZ) of South; Chengdu (CD) of Southwest (Fig. S1). The majority (11 of total 18) of the cities are provincial capitals or are under direct administration by the central government (BJ and SH). The other seven cities (DL, CZ, LY, QD, XM, SuZ, and SZ) are equivalent to provincial capitals in terms of economic development and population sizes. The sum of the population of all the cities is 174.5 million, representing about 13% of entire population of the nation.

In total, wastewater samples were collected from 36 STPs in the above cities. In most cities, two or three STPs were chosen for sample collection. In LZ, SH, WH, and GZ, however, only one STP in each city was sampled. Most sampled STPs treat wastewater from the urban centers of the cities. The population served by the STPs totals 26.29 million, representing about 21% of the total population of the cities and 2.0% of the population of the entire country. The STPs are named as BJ-1 (first STP of Beijing), SuZ-2 (second STP of Suzhou), etc.

Wastewater was collected during two sampling campaigns. Sampling at LZ, XA, WH, LY, SH, and XM were performed between early August and mid-September of 2014, whereas samples from other cities were collected between May and September of 2015. Each STP was sampled for two days (typically one weekend day and one weekday) by collecting 24-h composite samples at the sewage inlets using autosamplers. STPs were asked to program the autosamplers to imbibe 100 mL of influent at an interval of 1 h. A few STPs (LZ-1, LY-1 and 2, XA-1 and 2, CZ 1–4) did not have autosamplers. At these STPs, 200 mL of wastewater was collected manually by plant staff every 2 or 4 h throughout the day and was combined to form a composite sample. Since the time-intervals during sampling at these STPs were large (2 or 4 h), the possibility that NPS pulses were missed could not be ruled out (Ort et al., 2010). However, manual sampling at shorter intervals was too demanding for the staff and so was not enforced.

At selected STPs, effluent samples were collected in the same manner and at same time as influent samples. Following collection, the