Occurrence and removal of illicit drugs in different wastewater treatment plants with different treatment techniques

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Research

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Abstract

Background

As a class of contaminants of emerging concern (CECs), illicit drugs should be taken into account in the water management because of their social and public health risks. Wastewater treatment plants (WWTPs) are usually considered as the source and sink of contaminants, and drug residues are observed in their effluents due to the inefficient removal of CECs. In this study, wastewater samples were collected from eight WWTPs in Changzhou City for assessment of the abuse of 12 illicit drugs in the city by Wastewater-based epidemiology (WBE) method.

Results

Drug concentrations ranged from <LOD-51.62 ng/L and <LOD-22.44 ng/L in influent and effluent samples, respectively. The highest removal rate of drugs was 79.0% in the WWTP which used sequencing batch reactor activated sludge (SBR) process method, while the lowest was found in the WWTP using anoxic oxic (A/O) process (47.0%), indicating that the drug removal rates were closely related to the treatment techniques. WBE method was applied to estimate the population normalized illicit drugs consumption. It demonstrated that methamphetamine (METH) was the most abused drug in Changzhou City, ranging from 0.16-20.65 mg/d/1000 inh, while other target drugs ranged from <LOD-1.52 mg/d/1000 inh. Consumption of cocaine (COC) and ecstasy was very low among the samples.

Conclusion

Overall, this research suggests that the SBR process is the best for removing illicit drugs. WBE can be readily to monitor the abuse of drugs in those regions, compared with traditional monitoring models. Much attention should be paid by regulatory and management communities to METH and KET abuse in Changzhou City.

Background

The consumption of illicit drugs has been a growing concern worldwide. World Drug Report of 2018 points out that more than 275 million residents around the world were taking drugs, with thousands of tons of illicit drugs consumed annually [1]. In China more than 2.4 million residents consumed drugs at least once in 2017 [2]. Ultimately, illicit drugs enter the wastewater system as unaltered forms or/and metabolites with human excrement after their consumption and excretion, or as aftermath of police interventions after the illegal discharges [3]. Studies on the occurrence of target compounds in raw waters from wastewater treatment plants (WWTPs) supply invaluable information on illicit drug using and consumer trends at local, national and international levels [3–6]. The method called “wastewater-based epidemiology (WBE)” [4] could assess the consumption of illicit drugs by local people, which has been confirmed by traditional approaches [7].

Illicit drugs may cause potential risk to aquatic organism and human health when they enter the natural water environment. The effluents from WWTPs were the principal source of illicit drugs in the surface water [8]. The elimination efficiency of illicit drugs varied compound by compound in WWTPs. For instance, the removal rate of amphetamine (AMP) and cocaine (COC) was more than 90%, while the removal efficiency of 3,4methylenedioxymethamphetamine (MDMA) or methamphetamine (METH) was below 50% [9, 10]. The majority of illicit drugs cannot be completely removed in the traditional WWTPs, and a great number of illicit drugs were able to get in the surface water, groundwater and drinking water sources with the discharged effluent [11].

In the present study we reported the detection of 12 illicit drugs in both influents and effluents from eight WWTPs using different treatment techniques in Changzhou City, east China. The total consumption amounts of target drugs in the sampling period were estimated using WBE. Furthermore, the removal rates of target analytes in the WWTPs were assessed, and the effect of various wastewater treatment techniques on the drugs removal was determined as well.

Materials And Methods

Reagents and chemicals

The target illicit drugs, including methamphetamine (METH), cocaine (COC), 3,4-methylenedioxymethamphetamine (MDMA), benzoylecgonine (BE), amphetamine (AMP), methadone (MET), norketamine (NK), codeine (COD), ketamine (KET), 3,4-methylenedioxyamphetamine (MDA), methcathinone (MC), heroin (HR), and methamphetamine- d_8 (METH- d_8) with purities greater than 98.2%, were purchased from Cerilliant Corporation (Round Rock, TX) (Fig. 1). Formic acid (FA) (99%) was obtained from Sigma-Aldrich (Steinheim, Germany) and ammonium hydroxide (NH_3H_2O) was obtained from J&K Scientific (Beijing, China). HPLC-grade methanol (MeOH) and acetonitrile (ACN) were obtained from Fisher Scientific (Poole, UK). Ultrapure water was acquired using a Milli-Q ultrapure water system (Millipore, Bedford, MA, USA).

Sample collection

Wastewater samples (all samples were collected on the same day and at 60 minute intervals (24 h composites) in a time scale) were taken from 500 mL both influents and effluents of 8 WWTPs in Changzhou. The main information of each WWTP was shown in Table 1. All samples were stored in polyethylene terephthalate bottles (adjust all water samples to pH=2, and Adjust all water samples to pH=2, then add 5 ng METH- d_8 and EDTA-2Na) transferred to laboratory in 4°C ice box, and treated within 24 h.

Sample preparation and extraction

The solid phase extraction (SPE) method was used to extract illicit drugs in the study which was similar to our previous work [12, 13]. Briefly, wastewater sample was filtered through glass microfiber filters (GF/C Whatman, 0.47 μ m), followed by SPE with Oasis MCX cartridges (60 mg, 3 cc) through a vacuum extraction manifold. With the addition of internal standards, wastewater samples were loaded on the cartridges which were preconditioned with successive 5 mL of methanol and 5 mL ultrapure water. After water loading, the MCX cartridge was rinsed by 6 mL ultrapure water, and drained by a vacuum for half an hour for removing excessive water. The target drugs were eluted from the cartridges by 6 mL 5% NH_3H_2O in ACN. The extract was concentrated with weak N_2 stream in the water bath at 40°C to dryness, and the volume was brought to 1 mL with 10% acetonitrile in water. Prior to the analysis with ultra-performance liquid chromatography equipped with tandem mass spectrometry (UPLC-MS/MS), the extracts were passed through a 0.22 μ m nylon syringe filter.

Instrumental analysis

Quantification of analytes was conducted with a Waters triple quadrupole mass spectrometer equipped with an electrospray ionization source under positive electrospray ionization (ESI+) and multiple-reaction monitoring (MRM) mode. The analytes were separated with an Acquity UPLC BEH C18 column (2.1 mm $\times$ 50 mm, 1.7 μ m particle size), and the column temperature was kept at 40°C during sample analysis. The Milli-Q water with 0.1% FA was used as

mobile phase A, and the ACN as mobile phase B. The velocity of flow was maintained at 0.45 mL/min, and the volume of injection was 5 µL. The elution gradient was starting with 98% of A for 0.5 min, then increased A to 50% gradually within 4.5 min, and then increased A to 98% at 4.6 min. The next process was to maintain A at 98% for 1.4 min, and then decreased A to 2% gradually within 6.2 min, and kept constant for 1.3 min to re-equilibrate before the injection of the next water sample. The total working time was 7.5 min. The ion spray voltage was 4.5 kV. The source temperature was 450°C. The collision gas pressure was 9.0 Psi. Other experimental parameters were listed in Table S1. The software MassLynx and TargetLynx V4.1 was used to acquire and process the data.

Quantification and quality control

To determine the accuracy and precision of the analytical approach, Milli-Q water and wastewater samples spiked with deuterated standards were treated with the same pretreatment method. Matrix effect was investigated by spiking the deuterated standards (5 µg/L) into wastewater samples before extraction. A 6-point calibration standard curve (0.1 - 10 µg/L) was conducted with correlation coefficient (R^2) greater than 0.99. A procedural blank and a quality control sample (2 µg/L) were injected between every 10 analyses. In the procedural blank the concentrations of target analytes were below the detection limits. The limit of detection (LOD) was calculated by the minimal detectable content (at signal/noise ratio of 3) of a drug from the 12 environmentally matrix-spiked extracts. The LODs for each compound were calculated by MassLynx and TargetLynx V4.1 (Waters, US) from the recovery data of each compound, which were ranging from 0.005 - 0.025 ng/L, with details featured in Table S2.

Wastewater based epidemiology

Wastewater based epidemiology (WBE) was an effective method to investigate the chemical consumption of the urban population. Combined with traditional survey method, WBE can provide real-time and objective data for drug related policy. WBE assesses daily per capita consumption of drugs by the measured concentration of target residues in population and wastewater, daily flow rate of WWTPs, and human metabolic factors (corrected relationship between target residues and actual drugs) in the service area of WWTPs [14].

The daily mass load of each compound into a certain WWTP was calculated with the equation as follows:

$$\text{Influent load of a chemical residue} \left(\frac{\text{mg}}{1000 * d} \right) = \frac{\text{Concentration of a illicit drug} \left(\frac{\text{ng}}{\text{L}} \right) * \text{Influent flow} \left(\frac{\text{L}}{\text{d}} \right)}{\text{Population served} / 1000} * \frac{1}{10^6}$$

The influent concentration of the illicit drug was experimentally determined. Average influent flow on every sampling day was provided by each WWTP. Similarly, WWTPs supplied population from serving community.

Results And Discussion

Illicit drugs in wastewater

Concentrations of 12 illicit drugs in both influents and effluents from 8 WWTPs were summarized in Table 2. METH, COC and KET were the most frequently observed compounds, which were found in all influent samples. The detection frequencies of AMP, MC, COD, HR, MET, MDMA, and MDA in influents were greater than 75%, whereas BE was only detected in the WWTP TNQ-2 (Table2). METH concentrations ranged from 1.28 to 51.6 ng/L and from <LOD to 22.4 ng/L in the influents and effluents, respectively. The lowest and highest average concentrations of METH were observed at WJQ-1 (1.20 ± 0.5 ng/L) and XBQ-1 (51.62 ± 3.5 ng/L), respectively. In general, METH concentrations in the present study were similar to the influent levels from WWTPs at Nanjing, Shanghai and Nanning cities in China

[15], slightly higher than in eastern Canada and Dutch sewage water [16], slightly lower than in UK WWTPs [17], and much lower than in WWTPs in Yinchuan, Xiamen and Shenzhen in China [14].

AMP concentrations were lower than LOD at XBQ-1, and the highest AMP concentration was detected at JTQ-1 (10.29 ± 1.2 ng/L). Positive correlations were discovered between METH and AMP concentrations ($r=0.88$). AMP is the main metabolite of METH and also the ingredient of Selegiline, the medicine for treating Parkinson's disease [18]. Studies have shown that the conversion ratio of METH to AMP after metabolism is between 4% and 7% [14]. It is logical to draw that when the concentration rate of AMP to METH was between 0.04-0.1, AMP was mostly derived from the transformation of METH. The ratio of concentration of AMP to METH was greater than 0.1 at most WWTPs in this study, indicating that the emergence of AMP was more likely to be related to the use of prescription drug Selegiline. This contrasted sharply with the status in European countries where more AMP relative to METH use was detected [19-21].

KET was observed in eight influent samples, and its concentrations were ranging from 0.78 - 2.50 ng/L, while NK was not detected in the influents (Table 2 and Fig. 2). Although KET was widely present in all WWTPs, its levels were as low as not able to generate detectable degradation product NK. Compared to the cities in those countries, NK was consistently observed in WWTPs in the southern cities of Shenzhen and Guangzhou, which was higher than in Beijing and Shanghai [22], implying the different consumption patterns of KET in different areas of China.

MDMA was observed in 75% of the samples. And the concentrations of MDMA ranged from 0.18-0.55 ng/L in influents and 0.18 - 0.67 ng/L in effluents. These concentrations were lower than many reported levels in countries with high consumption of MDMA, such as the US (70 ng/L) [23], UK (13.9 ng/L) [17] and Spain (180 ng/L) [24]. Compared with those cities, Changzhou is a relatively small area with less entertainment places, and the detected MDMA concentrations were nearly 100 times lower than in European countries. Similar to MDMA, low concentration of MDA was observed for 0.24-4.85 ng/L. The concentration range of COC is 0.18-0.75 ng/L, which is far lower than the influent concentration of UK WWTPs (5.1-208.9 ng/L) [25] and Canada WWTPs (289-823 ng/L) [26]. A comparative study was conducted in 9 WWTPs in Beijing, Guangzhou, Shenzhen and Shanghai in China [27], indicating that the illicit drug use pattern in China was different from European countries. In China, the use of METH and KET was the main concern, while the most popular ones in European countries were COC and MDMA.

MET was observed in more than 50% of both influents and effluents wastewater samples. Concentrations of MET in the influent were in the range of $\leq$ LOD-1.24 ng/L and in the effluent for $\leq$ LOD-0.18 ng/L. In this study, the concentrations of MET were lower than the reported levels in other countries, such as the US (62 ng/L) [18], Croatia (94 ng/L) [15] and Belgium (16 ng/L) [22].

Removal of illicit drugs from WWTPs

The removal efficiency of target analytes depends strongly on the wastewater treatment techniques. A summary of the removal efficiency of each WWTP was presented in Figure 3. In this study, the treatment techniques of the eight WWTPs included anaerobic anoxic oxic (A^2/O) process, anoxic oxic (A/O) process and sequencing batch reactor activated sludge (SBR) process. SBR process was able to effectively remove illicit drugs from water, with the highest removal rate for the 12 target drugs of 79%, followed by the A^2/O process (73%). In the SBR process, illicit drugs were firstly eliminated in the primary sedimentation tank. By mixing and aerating the wastewater with SBR process, the organic pollutants in the wastewater were decomposed, and the removal efficiency could reach more than 70%.

The negative removal of some illicit drugs was also observed in the WWTPs, with the highest negative removal rates of MC and MDMA up to -155.9% and -60.7%, respectively. Negative removal was also reported for KET [16, 20, 28] and

other target drugs [18], which may be bound up with the increased transformation of precursor compounds or parent compounds, hydraulic residence time, and/or desorption from suspended solids in the wastewater treatment processes [19, 29].

BE was detected only in the influent of TNQ-2. BE is the major metabolite of COC. COC concentrations were relatively low in all 8 wastewater treatment plants, and the removal rate of COC in the sewage treatment process was basically below 50% [24]. This result was inconsistent with the previous study that COC was easily metabolized into BE and after human metabolism, only 1% of them was excreted from urine in the form of COC, and 25% -45% was excreted in the form of BE [4, 30]. METH, MET and MDA were effectively removed in different WWTPs, with removal rates ranging from 51.3% to 100%. Conversely, MDMA displayed negative removal in four WWTPs in this study. This phenomenon was possibly related to its highly recalcitrant property in wastewater and longer half-life of MDMA compared with other target drugs, which may elevate both the persistence of MDMA in wastewater and resistance to biological processes in the secondary treatment procedures [31].

Mean loads of illicit drugs

Among the 8 WWTPs, LYS-1 receives domestic sewage, XBQ-3 and JTQ-1 receive both domestic sewage and industrial sewage, and the rest 5 WWTPs receive industrial sewage only.

The mass loads of illicit drugs were ranged from 0.01 mg/d/1000 inh (MDMA in LYS-1) to 20.65 mg/d/1000 inh (METH in XBQ-1) (Fig. 4). Average loads of METH, AMP, KET, COD, MDA and MC in the eight WWTPs were 5.89 ± 8.74 , 0.84 ± 0.62 , 0.34 ± 0.41 , 0.48 ± 0.76 , 0.42 ± 0.39 and 0.41 ± 0.36 mg/d/1000 inh, respectively (Table 3). No obvious trend was observed regarding the average loads in the WWTPs relative to loads in 24 h.

High METH loads were found in XBQ-1 (20.65 mg/d/1000 inh) and XBQ-3 (18.99 mg/d/1000 inh). These loads were lower than those of wastewater samples (1500-1800 mg/d/1000 inh) in Australia [6] and other cities in China such as Haerbin (181.20 ± 6.50 mg/d/1000 inh) [19], Yinchuan (148.00 ± 145.20 mg/d/1000 inh) [15], and the mean METH load in WWTPs from 18 cities in China was 67.80 ± 45.2 mg/d/1000 inh, which was 3-fold higher than the mean load in this study [15].

COC and MDMA consumption was much lower than METH in this study, ranging from 0.02 to 0.15 mg/d/1000 inh for COC and 0.02-0.16 mg/d/1000 inh for MDMA. The consumption of COC and MDMA estimated in the present study was lower than 20.00-200.00 mg/d/1000 inh and 5.00-50.00 mg/d/1000 inh, respectively, in WWTPs of South-East Queensland in Australia. The average loading of MC was < LOD -0.92 mg/d/1000 inh, which was lower than 0.50 mg/d/1000 inh in Great Britain and 1.0 mg/d/1000 inh in Italy [32]. The average loading of MET was 0.09 ± 0.06 mg/d/1000 inh, far lower than Sweden (0.50-29.00 mg/d/1000 inh) [33] and Finland (1.2-9.5 mg/d/1000 inh) [20].

The average daily load of MDA and MDMA was < LOD - 1.10 and < LOD - 0.16 mg/d/1000 inh, respectively. The measured level was comparable with other Chinese cities for Shenzhen and Guangzhou [22], but was much lower than the MDMA load of 5-41 mg/d/1000 inh in the working days of the 25 WWTPs in France [6]. The maximum load of HR was 0.98 mg/d/1000 inh, which was much lower than the average HR load of 61 mg/d/1000 inh in the Ebro River Basin [18]. HR load in Guangzhou and Shenzhen in China was less than 4.0 mg/d/1000 inh [15], while the HR load in western cities of China was higher. The daily load of COD was < LOD - 2.01 mg/d/1000 inh, which was basically consistent with the average COD load of 5.7 mg/d/1000 inh in South Korean [25], far low than the UK [24], with corresponding load of 565 mg/d/1000 inh.

Although COD and MET were detected in most WWTPs in this study, the detection concentrations were significantly lower than European cities with the estimated COD load of 2-1998 mg/d/1000 inh [3]. MET and COD are used as controlled medicines in China [34] (In 2018, the State Drug Administration listed COD as the prohibited substance for adolescents and children). In Europe however, MET is used as an alternative medicine for methadone oral solutions. In most EU countries, COD can be used legally. Drugs containing codeine are approved by national procedures and sold as prescription or over-the-counter drugs in different prescriptions [34].

Conclusions

In the present study, we investigated the occurrence and elimination of 12 illicit drugs and their metabolites from 8 wastewater treatment plants in Changzhou City. METH, AMP, KET, MDMA and MET were the dominant drugs in these WWTPs, with higher concentrations than other drugs. Among the treatment techniques, SBR process was efficient for removal of illicit drugs, while the removal efficiency of target drugs by A/O process was low. Results from wastewater-based epidemiology showed that METH was the most consumed illicit drug, which should draw much attention by regulatory and management communities.

Abbreviations

METH: methamphetamine, COC: cocaine, BE: benzoylecgonine, MDMA: 3,4-methylenedioxymethamphetamine, AMP: amphetamine, MET: methadone, NK: norketamine, COD: codeine, KET: ketamine, MDA: 3,4-methylenedioxyamphetamine, MC: methcathinone, HR: heroin, WWTPs: wastewater treatment plants, A²/O: anaerobic anoxic oxic process, A/O: anoxic oxic process, WBE: wastewater based epidemiology

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and material

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

YD, CG and HZ involved in the experiments and manuscript writing, XY, LC and DW were responsible for the data analysis. JX contributed to the study design and manuscript correction. All authors read and approved the final manuscript.

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References

1. UNODC (2018) Global overview of drug demand and supply, <http://www.unodc.org/wdr2018/>
2. CNNCC (2018) Report on the drug situation in China, <http://www.mps.gov.cn/n6557558/c6535096/content.html>
3. Thomas KV, Bijlsma L, Castiglioni S, Adrian C, Erik E, Roman G, Félix H, Sara K, Barbara KH, Richard H, Lindberg, Miren L A, Axel M, Christoph O, Yolanda P, José BQ, Malcolm R, Jörg R, Senka T, van Nuijs ALN, Pim V (2012) Comparing illicit drug use in 19 European cities through sewage analysis. *Sci Total Environ* 432:432–439
4. Zuccato E, Chiabrando C, Castiglioni S, Renzo B, Roberto F (2008) Estimating community drug abuse by wastewater analysis. *Environ Health Perspect* 116:1027–1032
5. van Nuijs ALN, Mougél JF, Tarcomnicu I, Bervoets L, Blust R, Jorens PG, Neelsae H, Covacia A (2011) A one year investigation of the occurrence of illicit drugs in wastewater from Brussels, Belgium. *J Environ Monit* 13(4):1008–1016
6. Nefau T, Karolak S, Castillo L, Boireau V, Levi Y (2013) Presence of illicit drugs and metabolites in influents and effluents of 25 sewage water treatment plants and map of drug consumption in France. *Sci Total Environ* 461–462:712–722
7. Reid MJ, Langford KH, Grung M, Gjerde H, Amundsen EJ, Morland J, Thomas KV (2012) Estimation of cocaine consumption in the community: a critical comparison of the results from three complimentary techniques. *BMJ Open* 2(6):e001637
8. Chiaia AC, Banta-Green C, Field J (2008) Eliminating solid phase extraction with large-volume injection LC/MS/MS: Analysis of illicit and legal drugs and human urine indicators in US wastewaters. *Environ Sci Technol* 42(23):8841–8848
9. Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ (2008) Multiresidue methods for the analysis of pharmaceuticals, personal care products and illicit drugs in surface water and wastewater by solid-phase extraction and ultra performance liquid chromatography-electrospray tandem mass spectrometry. *Anal Bioanal Chem* 391(4):1293–1308
10. Boleda MR, Galceran MT, Ventura F (2009) Monitoring of opiates, cannabinoids and their metabolites in wastewater, surface water and finished water in Catalonia, Spain. *Water Res* 43(4):1126–1136
11. Daughton CG (2001) Illicit drugs in municipal sewage. *ACS Symposium Series* 791:348–364
12. Guo C, Zhang T, Hou S, Lv JP, Zhang Y, Wu FC, Hua ZD, Meng W, Zhang H, Xu J (2017) Investigation and application of a new passive sampling technique for in situ monitoring of illicit drugs in waste waters and rivers. *Environ Sci Technol* 51(6):9101–9108
13. Zhang Y, Zhang T, Guo C, Lv JP, Hua ZD, Hou S, Zhang Y, Meng W, Xu J (2017) Drugs of abuse and their metabolites in the urban rivers of Beijing, China: Occurrence, distribution, and potential environmental risk. *Sci Total Environ* 579:305–313

14. Li J, Hou L, Du P, Yang J, Li KY, Xu ZQ, Wang CC, Zhang HF, Li XQ (2014) Estimation of amphetamine and methamphetamine uses in Beijing through sewage-based analysis. *Sci Total Environ* 490:724-732
15. Du P, Li K, Li J, Xu ZQ, Fu XF, Yang J, Zhang HF, Li XQ (2015) Methamphetamine and ketamine use in major Chinese cities, a nationwide reconnaissance through sewage-based epidemiology. *Water Res* 84:76-84
16. Metcalfe C, Tindale K, Li H, Rodayan A, Yargeau V (2010) Illicit drugs in Canadian municipal wastewater and estimates of community drug use. *Environ Pollut* 158(10):3179–3185
17. Baker DR, Kasprzyk-Hordern B (2013) Spatial and temporal occurrence of pharmaceuticals and illicit drugs in the aqueous environment and during wastewater treatment: New developments. *Sci Total Environ* 454-455:442-456
18. Postigo C, López de Alda MJ, Barceló D (2010) Drugs of abuse and their metabolites in the Ebro River basin: Occurrence in sewage and surface water, sewage treatment plants removal efficiency, and collective drug usage estimation. *Environ Int* 36(1):75–84
19. Andrés-Costa MJ, Rubio-López N, Morales Suárez-Varela M, Pico Y (2014) Occurrence and removal of drugs of abuse in Wastewater Treatment Plants of Valencia (Spain). *Environ Pollut* 194:152-162
20. Östman M, Fick J, Näsström E, Lindberg RH (2014) A snapshot of illicit drug use in Sweden acquired through sewage water analysis. *Sci Total Environ* 472:862-871
21. González-Mariño I, Gracia-Lor E, Rousis NI, Castrignanò E, Thomas KV, Quintana JB, Kasprzyk-Hordern B, Zuccato E, Castiglioni S (2016) Wastewater-based epidemiology to monitor synthetic cathinones use in different European countries. *Environ Sci Technol* 50(18):10089-10096
22. Khan U, van Nuijs ALN, Li J, Maho W, Du P, Li KY, Hou LL, Zhang JY, Meng XZ, Li XQ, Covaci A (2014) Application of a sewage-based approach to assess the use of ten illicit drugs in four Chinese megacities. *Sci Total Environ* 487:710-721
23. Kinyua J, Anderson TA (2012) Temporal analysis of the cocaine metabolite benzoylecgonine in wastewater to estimate community drug use. *J Forensic Sci* 57(7):1349-1353
24. Baker DR, Očenášková V, Křiváková M, Kasprzyk-Hordern B (2012) Drugs of abuse in wastewater and suspended particulate matter-Further developments in sewage epidemiology. *Environ Int* 48:28–38
25. Kim KY, Lai FY, Kim HY, Thai PK, Mueller JF, Oh JE (2015) The first application of wastewater-based drug epidemiology in five South Korean cities. *Sci Total Environ* 524–525:440–446
26. Boleda MR, Huerta-Fontela M, Ventura F, Galceran T (2011) Evaluation of the presence of drugs of abuse in tap waters. *Chemosphere* 84(11): 1601-1607
27. Vazquez-Roig p, Andreu V, Blasco C, Picó Y (2010) SPE and LC-MS /MS determination of 14 illicit drugs in surface waters from the Natural Park of L'Albufera (València Spain). *Anal Bioanal Chem* 397(7):2851-2864
28. Fernandez-Fontaina E, Omil F, Lema JM, Carballa M (2012) Influence of nitrifying conditions on the biodegradation and sorption of emerging micropollutants. *Water Res* 46:5434–5444
29. Subedi B, Kannan K (2014) Mass Loading and removal of select Illicit drugs in two wastewater treatment plants in New York state and estimation of illicit drug usage in communities through wastewater analysis. *Environ Sci Technol* 48(12):6661-6670
30. Castiglioni S, Bijlsma L, Covaci A, Emke E, Hernández F, Reid M, Ort C T, Thomas KV, van Nuijs ALN, Voogt P, Zuccato E (2013) Evaluation of uncertainties associated with the determination of community drug use through the measurement of sewage drug biomarkers. *Environ Sci Technol* 47(3):1452-1460
31. Evans SE, Bagnall J, Kasprzyk-Hordern B (2016) Enantioselective degradation of amphetamine-like environmental micropollutants (amphetamine, methamphetamine, MDMA and MDA) in urban water. *Environ Pollut* 215:154-163

32. van Nuijs ALN, Tarcomnicu I, Bervoets L, Blust R, Jorens PG, Neels H, Covaci A (2009) Analysis of drugs of abuse in wastewater by hydrophilic interaction liquid chromatography-tandem mass spectrometry. *Anal Bioanal Chem* 395(3):819-828
33. Banta-Green CJ, Field JA, Chiaia AC, Sudakin DL, Power L, Montigny L (2009) The spatial epidemiology of cocaine, methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA) use: A demonstration using a population measure of community drug load derived from municipal wastewater. *Addiction* 104:1874-1880
34. INCB (2015) Report of the international narcotics control board for 2014, http://www.incb.org/documents/Publications/AnnualReports/AR2014/AR_2014_E.pdf

Tables

Table1 The main information of 8 WWTPs

	TNQ-1	TNQ-2	XBQ-1	XBQ-2	XBQ-3	WJQ-1	JTQ-1	LYS-1
Treatment process	SBR process	SBR process	A ² O	A\O	A ² O	A\O	A ² O	A ² O
Average water intake (m ³ /d)	15000	25000	160000	3000	80000	25000	35000	70000
People (million)	0.08	0.30	0.30	0.01	0.15	0.13	0.25	0.65
Influent characteristics								
COD (mg/L)	1123	780	255	1185	260	971	265	247
N (mg/L)	21.46	18.74	36.1	88	31.54	12.3	35	39.62
P (mg/L)	4.65	2.08	4.41	-	4.46	3.02	3.42	6.95
NH ₄ (mg/L)	21.46	18.74	23	88	27.3	12.3	30	28
Effluent characteristics								
COD (mg/L)	178	150	41	51.3	32.8	60	33	41
N (mg/L)	5.43	4.17	8.78	24.7	8.26	2	10.89	8.83
P (mg/L)	1.69	0.95	0.15	-	0.11	0.49	0.25	0.17
NH ₄ (mg/L)	5.43	4.17	2	24.7	2	2	2	2

Table2 Concentration and frequency of detection of the target illicit drugs and metabolites in the influent and effluent (ng/L).

Compound		TNQ-1	TNQ-2	XBQ-1	XBQ-2	XBQ-3	WJQ-1	JTQ-1	LYS-1	Freq. (%)
METH	influent	5.13	1.95	51.62	1.21	35.61	1.20	6.58	45.08	100.00
	effluent	0.38	0.47	16.59	∅LOD	8.24	0.74	19.71	22.44	87.50
AMP	influent	8.11	1.43	∅LOD	2.22	2.82	1.19	10.29	4.27	87.50
	effluent	∅LOD	1.03	1.06	∅LOD	∅LOD	1.06	1.22	1.29	62.50
KET	influent	1.72	0.78	0.78	0.90	2.50	1.05	0.87	0.96	100.00
	effluent	∅LOD	0.19	0.86	0.35	1.21	0.70	0.94	1.01	87.50
NK	influent	0.38	∅LOD	0.73	0.34	∅LOD	0.23	0.16	∅LOD	62.50
	effluent	0.58	0.27	0.36	0.31	∅LOD	0.18	0.33	0.18	87.50
COD	influent	10.71	∅LOD	∅LOD	0.80	0.81	0.40	0.42	0.94	75.00
	effluent	0.00	0.42	0.34	0.61	∅LOD	0.46	0.30	0.39	75.00
HR	influent	0.00	0.38	0.30	0.74	0.37	0.46	6.99	∅LOD	75.00
	effluent	1.53	0.34	0.42	0.69	0.34	0.43	1.81	0.40	100.00
MET	influent	0.44	1.24	0.14	0.60	∅LOD	0.72	∅LOD	0.09	75.00
	effluent	∅LOD	0.09	∅LOD	0.19	∅LOD	0.10	∅LOD	0.10	50.00
COC	influent	0.75	0.38	0.18	0.51	0.18	0.30	0.19	0.21	100.00
	effluent	0.49	0.19	0.18	0.40	0.18	0.20	0.19	0.19	0.00
BE	influent	∅LOD	0.19	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	12.50
	effluent	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD	∅LOD
MDMA	influent	0.48	0.00	0.30	0.55	0.00	0.21	0.26	0.18	75.00
	effluent	0.67	0.18	0.49	∅LOD	0.21	0.22	∅LOD	0.19	75.00
MDA	influent	1.75	0.24	2.74	∅LOD	∅LOD	1.10	4.85	2.18	75.00
	effluent	0.60	∅LOD	0.24	∅LOD	0.46	0.25	2.36	0.39	75.00
MC	influent	0.61	0.28	2.16	0.95	∅LOD	2.69	6.58	1.62	87.50
	effluent	0.50	0.67	0.18	1.23	0.31	0.19	∅LOD	0.58	87.50

Figures

Amphetamine

Methamphetamine

Methcathinone

MDA

MDMA

Norketamine

Ketamine

Benzoylecgonine

Codeine

Cocaine

Methadone

Heroin

Figure 1

Structure of 12 target illicit drugs in this study

Figure 2

Average concentrations of target analytes over 24 hours period in wastewater influent and effluent of 8 WWTPs.

Figure 3

Comparison of removal efficiency of illicit drugs in the 8 WWTPs.

Figure 4

The estimated illicit drugs consumption per inhabitant in eight wastewater treatment plants in Changzhou City.

Supplementary Files

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