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Biodegradation of methamphetamine and ketamine in aquatic ecosystem and associated shift in bacterial community

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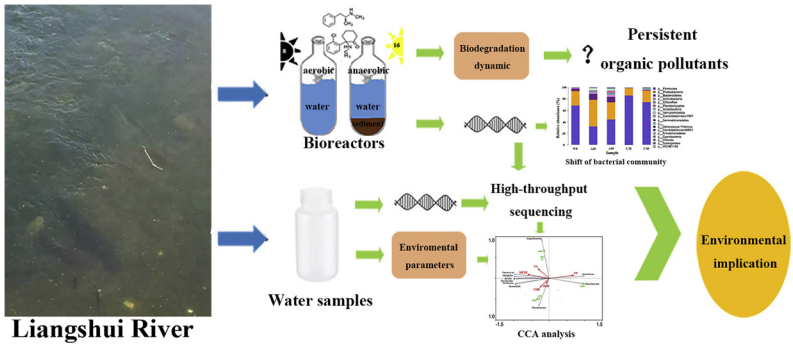
GRAPHICAL ABSTRACT



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ABSTRACT

Methamphetamine (METH) and ketamine (KET) are widely detected in surface waters and thus may pose threat to aquatic organisms. However, their degradation in aquatic systems and the effects on bacterial community were unknown. The present study investigated the biodegradation process of METH and KET in river waters and sediments. Three microcosms were examined over 40-days' incubation under (i) aerobic and illumination conditions, (ii) anaerobic condition exposed to light, (iii) anaerobic-dark condition. Statistically significant biodegradation of METH and KET (1 mg L^{-1}) was observed in all treatments. The half-lives under the examined conditions indicate that the two drugs were refractory in aquatic environment. Moreover, there were no pronounced absorption and photolysis observed in this work. Illumina MiSeq sequencing analysis revealed that Methylophilaceae, Saprospiraceae, WCHB1–69, Desulfobulbaceae, Porphyromonadaceae, FamilyXI, Peptococcaceae, and Rhizobiaceae were the predominant candidatus families during KET and METH biodegradation, and the preponderance would impair other microorganisms' prosperity since them were scarcely detected in the wild. Meanwhile, canonical correlation analysis (CCA) indicates that METH as an environmental factor may affect bacterial community structure in field water samples.

1. Introduction

Abuse of illicit drugs has resulted in their widespread occurrence in various aquatic environments [1]. The major sources included hospital wastewater, municipal wastewater treatment plant effluent, and direct sewage discharge [2]. In China, methamphetamine (METH) and ketamine (KET) were the predominant illicit drugs in surface waters. The concentrations in Taiwan were up to 405 ng L^{-1} for METH and

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341 ng $L^{-1}$for KET, while the levels were up to 239 ng L^{-1} for METH and 275 ng $L^{-1}$for KET in mainland China [3,4].

The wide detection of METH and KET in surface waters may pose risks to human health and the environment. METH can evoke oxidative stress and neurotoxicity of mammals with super-clinical doses [5], whereas KET (a non-competitive inhibitor of N-methyl-D-Aspartate (NMDA) receptors) may interfere with the central nervous system, and induce hallucinations [6,7]. Moreover, exposure to METH and KET at environmentally relevant levels could alter the physiological function (e.g., heart rate, locomotion and hatching time) and the P_{53} regulated apoptosis of medaka larva [8,9].

Hence, it is of great importance to understand the fate of METH and KET during wastewater treatment and in aquatic environment [10,11]. Removal of METH and KET in traditional treatment processes have been examined by several research groups. Li et al. [2] reported that METH and KET couldn't be completely removed during the conventional wastewater treatment, and the removal rates were 80% and 50%, respectively. Kasprzyk-Hordern et al. [12] examined the removal of METH during different sewage treatment stages, and revealed that the secondary treatment with activated sludge removed greater amounts of target compounds. The simulated active sludge microcosm experiments verified that the half-life of S-(+)-Methamphetamine was 14.3 h, and no reduction of R-(-)-Methamphetamine was detected with 24 h treatment. Lin et al. [13] reported that these two drugs were completely degraded by UV/TiO_2 or ZnO with 15 min illumination. Meanwhile, no evaporation and absorption process were observed. The photocatalytic degradation of METH with UV/TiO_2 was impacted by pH, temperature, initial concentration, and catalyst content. All organic carbon (100%) was ultimately mineralized to CO_2 during the process [14].

However, there were only two reports in the literature on the attenuation of METH and KET in surface waters. Kasprzyk-Hordern et al. [15] documented that biodegradation of METH in simulated river water reactors was less than 15% with illumination after 15 days. Meanwhile, the stereo-selectivity of METH was observed during incubation under biotic condition. However, organic pollutants in surface water may well be degraded by complex bacterial community in sediment [16,17]. Hence, it seems that only considering degradation by water bacteria for short-term incubation (15 days) is insufficient to assess the fate of METH in aquatic ecosystem. Lin et al. [18] conducted a photolysis experiment of KET using sunlight simulator. The half-life of KET in river samples spiked with CO_2 and nitrate was 12.6 h. The toxicity of dehydronorketamine (DNK) as the major by-product cannot be ignored. However, to date, the biodegradation of KET in surface water has not been examined clear. Meanwhile, an effective removal of KET in water or sediment is crucial for mitigating its toxicity risk on aquatic organisms. In addition, the shift of bacterial community associated with the biodegradation process of the two drugs was unclear. The alteration of microbial community structure is crucial for the ecosystem [19].

The objective of this work was to examine degradation of METH and KET by surface water and sediment microorganisms. Experiments were performed under aerobic and anaerobic conditions, with or without illumination. The composition of bacteria community associated with METH and KET degradation process was characterized using high-throughput sequencing. In recent years, high-throughput sequencing, especially Illumina MiSeq platform has been widely used to study the microbial populations in varying environmental samples [20,21]. This technique can not only detect rare bacterial species, but also yield detailed information of community shift. However, it has been rarely used to characterize bacteria composition during pollutant biodegradation [22]. The micro-community in field water samples containing METH was also detected to verify whether METH was a major factor using canonical correlation analysis (CCA). This is to our knowledge the first study to evaluate whether METH and KET were refractory in aquatic environment. The bacterial families responsible for degradation were identified, and the potential eco-risk during biodegradation was also proposed.

2. Methods and materials

2.1. Sampling and experiments setup

The surface water and sediment samples used in biodegradation experiments were collected from the Liangshui River (Fig. S1). The Liangshui River originates from the Shijinshan district and flows through Fengtai, Daxing, and Tongzhou districts in Beijing. Twelve samples (LSH1-12) were collected along the river on July 15th, 2015. METH in Liangshui River was widely detected. The concentration in water was 1.22–35.35 ng L^{-1}, and the level in sediment was 0.06-1.83 ngg^{-1} [3]. The concentration of KET in Liangshui River were 1.0–3.6 ng L^{-1} in water, and 0.05-0.12 ngg^{-1} in sediments. The water samples from all 12 points were partially pooled with the same volume and then filtered through 0.22 μm cellulose acetate filter (2 L each). The filter membranes that concentrated the biomass were stored at 4 ℃ until use. The sediment samples from all 12 points were dried, homogenized, sieved through 0.15 mm screen in anaerobic bench to eliminate the effect by oxygen, and then stored at 4 ℃ until use. The river sediments were slightly acidic (pH 5.6). Dissolved organic carbon (DOC) content was 4.3 gkg^{-1}. The mineral salt medium (pH 7.0) used in the experiments comprised (gL^{-1}): NH_4Cl (0.1), NaCl (3.98), $MgCl_2{\cdot}6H_2O$ (0.4), $MgSO_4{\cdot}7H_2O$ (0.53), $CaCl_2$ (0.038), KCl (0.11), $NaHCO_3$ (0.005), NaBr (0.013). The hydrochloride salts of methamphetamine (METH), amphetamine (AMP), ketamine (ket), and norketamine (norKET) as well as the deuterated internal standards (METH-d_8, AMP-d_8, KET-d_4, and norKET-d_4) (percent purity: 99%) were purchased from Cerilliant (Round Rock, TX, USA). All the other chemicals were obtained from Beijing Chemical Works (Beijing, China).

The biodegradation microcosm experiments consisted of 80 mL sterilized mineral salt medium and were performed in triplicate for every treatment under following conditions: i) aerobic-light treatment groups (illumination duration 18 h/24 h): (A) bioreactor: one piece of filter with the biomass + 1 mg L^{-1} METH and KET; (B)abiotic-control: one piece of filter with the biomass treated by sterilization + 1 mg L^{-1} METH and KET; (C) bio-control: one piece of filter with the biomass; ii) anaerobic-light treatment groups (illumination duration 18 h/24 h): (D) bioreactor: 8 g sediments + 1 mg L^{-1} METH and KET; (E) abiotic-control: 8 g sterilized sediments + 1 mg L^{-1} METH and KET; (F) bio-control: 8 g sediments; iii) anaerobic-dark treatment groups: (G) bioreactor: 8 g sediments + 1 mg L^{-1} METH and KET; (H)abiotic-control: 8 g sterilized sediments + 1 mg L^{-1} METH and KET; (I) bio-control: 8 g sediments. The measured concentrations of METH and KET were 52–55% and 72–80% compared with their nominal values, respectively (Table S3 and Table S4).

Silk mouth bottle (150 mL) was used as container for aerobic treatment groups in this work. The dissolved oxygen (DO) contents were measured periodically using portable dissolved oxygen meter (OxiCal-CX, WTW, Germany). The operation was performed in superclean bench. The receptacle for anaerobic treatment groups was serum bottle (150 mL) spiked with resazurin (0.001 g L^{-1}) as indicator and $NaNO_3$ (20 mmolL^{-1}) as electron acceptor. The operation was performed in anaerobic table. The daylight simulation was operated with Osram 400 W cold light lamp. The sterile controls were obtained by autoclaving at 120℃ three times (20 min for every time, three successive days), and then 2% sodium azide was added to inhibit the proliferation of bacteria. Microcosms were incubated at 28℃ on a horizontal shaker (140 rpm) for 40 days.

Five out of twelve sampling points (LSH 2, 3, 5, 6, 7) were selected as typical samples to analyze the community (Fig. S1). The water samples (2 L each) were filtered in triplicates through 0.22 μm cellulose acetate filter. The filters were then stored at −80℃until high-throughput sequencing. The hydrochemical parameters of water samples were showed in Table S1.