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Identification of nitrosamine precursors from urban drainage during storm events: A case study in southern China

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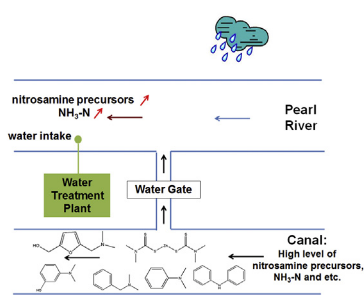
HIGHLIGHTS

- Nitrosamine (NA) precursors from drainage during storm event was firstly investigated.
- Formation potential (FP) of total NAs in storm drainage were about 100 ng/L.
- Powdered activated carbon removed 52% of NA FP while conventional process removed 10%.
- Ziram was screened as a new NA precursor via chloramination among six NA precursors.

GRAPHICAL ABSTRACT



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ABSTRACT

The drinking water sources of many cities in southern China are frequently contaminated by upstream urban drainage during storm events, which brings high concentrations of *N*-nitrosamine (NA) precursors and poses a threat to the safety of drinking water. We conducted two sampling campaigns during the heavy rain season in 2015 in one representative city in southern China. We detected that the concentration of *N*-nitrosodimethylamine formation potential (NDMA FP) in urban drainage during two storm events was 80–115 ng/L and the total formation potential concentration of nine nitrosamines (TNA_9 FP) was 145–165 ng/L. To address the deteriorated water quality, 30 mg/L of powdered activated carbon (PAC) was fed into the water intake. PAC adsorption alone could remove 52% of NDMA FP and 52% of TNA FP, while the subsequent conventional process only removed 8% of TNA FP. We isolated six chemicals (*N*,*N*-benzyldimethylamine, 5-[(dimethylamino)methyl]-2-furanmethanol, *N*,*N*-dimethyl-3-aminophenol, *N*,*N*-dimethylethylamine, Ziram, and *N*,*N*-dimethylaniline) and confirmed them to be NA precursors. Among these NA precursors, Ziram was identified for the first time as a NA precursor that is formed via chloramination; its molar yield for NDMA was 6.73 ± 0.40%.

1. Introduction

Many cities in China experience frequent flooding during the rainy season (Che et al., 2013; Xie, 2013). Urban drainage systems were designed and built dozens of years ago and cannot sufficiently accommodate the large amounts of storm runoff, which has

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increased in recent years as a result of rapid urban development and climate change (Peng et al., 2015). This has led to high amounts of stormwater being directly discharged into water bodies. The first flush of stormwater, i.e. the first about 30 min of precipitation, is generally heavily contaminated by organic matter, suspended solids, ammonia nitrogen (NH_3–N), heavy metals, and odorants (Sansalone and Cristina, 2004; Deng et al., 2009; Li et al., 2012b). Many Chinese cities also face the problem of the so-called "black and smell water body", which refers to an urban river, lake, or pond that is heavily contaminated by the uncontrolled domestic and industrial waste discharge (Li et al., 2012b; Xu et al., 2015). The "black and smell water" will eventually reach a receiving water body via the storm drainage. Thus, water that is transported through urban drainage systems during storm events to receiving water bodies will significantly deteriorate downstream water quality.

As many cities in China rely on rivers as their water source, urban drainage during storm events will significantly impact the safety of drinking water. In addition to the aforementioned contaminants, some emerging contaminants, such as *N*-nitrosamine (NA) precursors, may also exist in urban drainage. When urban drainage enters the source water of water treatment plants (WTPs), the high concentration of ammonia in the drainage water reacts with chlorine disinfectant to rapidly form chloramines. The de facto chloramination process will yield high concentrations of NAs.

The basic strategies to control NA formation in drinking water include the removal or destruction of NA precursors and optimization of conditions for chloramination (Liao et al., 2015b). Granular activated carbon (GAC) is an effective and practical technology used to remove NDMA precursors in source water (Hanigan et al., 2012; Krasner et al., 2013; Liao et al., 2014), so do oxidation by free chlorination, ozonation, or other processes (Krasner et al., 2013; Liao et al., 2014). Chen et al. (2015) conducted experiments on the adsorption of powdered activated carbon (PAC) to different types of water samples and the model NDMA precursors, ranitidine and chlorpheniramine. Results indicated that the removal of NDMA precursors by PAC adsorption is pH-dependent and site-specific.

Previous studies on the identification of NA precursors have produced a long list of such precursors, including secondary amines (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Wang et al., 2011), certain water treatment polymers (Padhye et al., 2011; Krasner et al., 2013), certain pharmaceutical and personal care products (PPCPs) (Shen and Andrews, 2011), certain pesticides or their degradation products (Schmidt and Brauch, 2008; Le Roux et al., 2011), wastewater treatment effluent organic matter (EfOM) (Mitch and Sedlak, 2004; Wang et al., 2014), certain industrial chemicals (Kosaka et al., 2010; Wang et al., 2014), algal organic matter (Li et al., 2012a), and natural organic matter (NOM) (Gerecke and Sedlak, 2003; Chen and Valentine, 2007). The list of known NA precursor chemicals is quite long and their occurrence in source waters is site-specific. Moreover, there are still many other NA precursors that have not been identified.

To assess the impact of urban drainage during storm events on drinking water safety, our team conducted two sampling campaigns in one representative city (City A) in southern China during the rainy season. We collected source water at the water intake, process effluent, and the finished water of affected WTPs. We measured the NAs and their formation potential (FP), as well as bulk water quality parameters. We assessed the efficiency of the conventional treatment process and the emergency treatment process (PAC adsorption) in treating the deterioration of source water quality due to drainage water. To better understand the NA sources, we also conducted further isolation of selective solid phase extraction (SPE) and screening procedure of time-of-flight mass spectrometer (TOF-MS) to identify the components contributing to the formation of NA precursors. The information could be used to develop a control strategy and technologies for the removal of NA from drinking water.

2. Methods and materials

2.1. Local climate

City A is located in the Pearl River delta on the Tropic of Cancer. The city has a tropical monsoon climate with hot humid summers (rainy season) and short warm winters (dry season). Its average annual temperature is 23.1 °C, and the temperature ranges from of 3.1–37.8 °C. Typhoons also influence this city greatly, with 4–6 typhoons occurring each year. The average annual precipitation is 1820 mm. Most rainfall occurs between April and September (80% of annual rainfall, Fig. S1). Heavy rain (>25 mm) occurs over 50 days annually.

2.2. Drainage system in City A

City A is located along the Pearl River. The local government built a drainage canal around the northern part of the city in the 1970s to prevent flooding. The canal connects the Pearl River with several gates to control the inside water level. Since the 1990s, the water quality in this canal has deteriorated drastically and the whole canal has been transformed into "black and smell" river as a result of the discharge of industrial wastewater, domestic sewage, and livestock breeding wastewater. Although the local government has made efforts to ban the discharge of industrial wastewater, uncontrolled domestic wastewater discharge remains a big problem. The water quality of this canal is worse than "Grade V", according to the Environmental Quality Standards for Surface Water of China (GB 3838-2002), which means the water is not suitable for any usage. During heavy rain, the water level of this canal rises rapidly, which threatens the security of the entire city. Thus, the gates must be opened to release the storm and urban drainage under those conditions, severely impacting the water quality downstream.

2.3. Affected water treatment plants

As the canal water is discharged into the main stream of the Pearl River, two downstream WTPs (WTP-A and WTP-B) will be affected by the deterioration of quality of the source water, as illustrated in Fig. 1a. WTP-A has a capacity of 180,000 m^3/d and WTP-B has a capacity of 800,000 m^3/d. These WTPs supply drinking water to about 6 million residents and hundreds of factories. The flowchart of these WTPs is illustrated in Fig. 1b. Both WTPs apply the conventional treatment process: coagulation, sedimentation, filtration, and disinfection.

As shown in Fig. S1, the WTPs are subject to source water of impaired quality during the 6-month rainy season, and the threat is especially high during the 50 days of heavy rain. During that time, it is expected that the canal water and impacted source water will have a strong smell and color, high concentrations of NH_3–N, high turbidity, and high concentrations of bulk organic matter. PAC adsorption is now widely applied across China as an emergency response technology to address water quality deterioration due to drainage events or organic chemical spills (Zhang et al., 2011; Zhang and Chen, 2009). In these WTPs, PAC is added to the water intake and the adsorption takes about 15 min to process inside the 2 km of pipe between the water intake and the distribution well of the WTPs. When the PAC-treated water reaches the WTP, alum coagulant is added to lower the turbidity and reduce the concentration of PAC particles. The PAC adsorption is subsequently halted during the coagulation and sedimentation processes.