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Monochloramine loss mechanisms and dissolved organic matter characterization in stormwater

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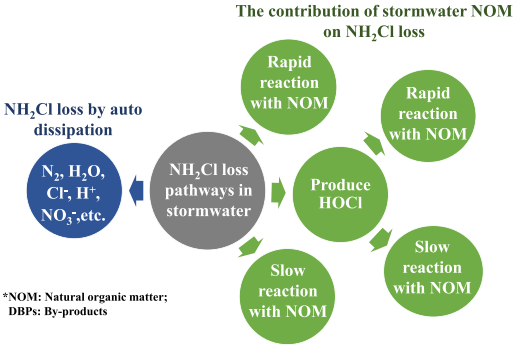
HIGHLIGHTS

- Active chlorine concentration was high in stormwater and can contaminate fresh water.
- Model was built to describe the monochloramine (NH_2Cl) decay in stormwater.
- Natural organic matter led to rapid and slow reactions with free chlorine and NH_2Cl.
- Humic substances were dominant in stormwater dissolved organic matter.

GRAPHICAL ABSTRACT



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ABSTRACT

Monochloramine (NH_2Cl) is widely used for secondary disinfection by water utilities. However, Edmonton field stormwater sampling results have shown that NH_2Cl, because of its long-lasting property, can cause stormwater contamination through outdoor potable water uses during the summer season. To protect water sources, it is important to understand NH_2Cl dissipation mechanisms in stormwater. Natural organic matter (NOM) is the dominant species that contributes to NH_2Cl decay in stormwater. In this research, it is proposed that NOM reacted with both NH_2Cl and free chlorine through rapid and long-term reactions during NH_2Cl dissipation. Based on this assumption, a kinetic model was developed and applied to estimate the NH_2Cl decay in real stormwater samples, and the modeling results matched experimental data well under all the conditions. Further, the stormwater dissolved organic matter (SWDOM) collected from different neighborhoods was analyzed by Fourier transform infrared (FTIR) and fluorescence excitation-emission matrix (EEM) techniques. Humic substances were found to be dominant in SWDOM, and the samples from different neighborhoods had similar organic constituents. After reaction with excess NH_2Cl, 25%–41% SWDOM fluorophores converted to inorganic components, while most of DOM remained in organic form. Humic substances as the major components in SWDON, are the dominant precursors of disinfection by-products in chloramination. Therefore, the potential reaction products of stormwater humic substances with NH_2Cl should also be of concern. This research provided a useful method to estimate the NH_2Cl dissipation in stormwater, and the methodology can also be applied for stormwater NH_2Cl decay studies in other cities. Further, it is believed the SWDOM analysis in this research will contribute to future studies of NH_2Cl NOM reaction mechanisms in both storm sewers and drinking water distribution systems.

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1. Introduction

Chloramination is widely used for drinking water secondary disinfection. Compared with free chlorine, monochloramine (NH_2Cl), the dominant species in chloramination, is less reactive and can provide a longer-lasting disinfection effect in drinking water distribution system (Brodtmann and Russo, 1979; Norman et al., 1980). However, the persistent NH_2Cl can lead to serious environmental problems through its introduction into storm sewers and thus fresh water sources. Outdoor tap water uses such as residential garden watering, lawn irrigation in parks, car washing at dealerships and industrial pressure vessel hydro-testing can all lead to the discharge of NH_2Cl into storm sewers. Our previous study showed that the total active chlorine (TAC) concentration in Edmonton municipal storm sewers varied from 0 to 0.77 mg/L under dry weather conditions during the summers of 2015 and 2016 (Zhang et al., 2018) which exceeded the Canadian Council of Ministers of the Environment guideline's recommended concentration of 0.02 mg/L in discharge effluent in most of times (Canadian Council of Ministers of the Environment, 2009). That is, once the chloraminated stormwater is discharged into fresh water sources, it may pose serious risks to the aquatic environment. To enhance the regulation of chloraminated tap water discharges, knowledge of NH_2Cl dissipation mechanisms in stormwater is important. However, although the NH_2Cl dissipation processes has been widely studied in drinking water distribution systems, little research has been undertaken to monitor NH_2Cl decay in storm sewer systems.

In drinking water distribution systems, NH_2Cl autodecomposition as well as reactions with water chemical components are considered the major NH_2Cl dissipation pathways (Vikesland et al., 2001; Zhang et al., 2017). NH_2Cl can autodecompose by a complex set of reactions that ultimately result in the oxidation of ammonia and the reduction of active chlorine. The rates of these reactions depend on the solution pH, alkalinity and initial NH_2Cl concentrations, as well as on the ratio of chlorine to ammonia nitrogen. Further, chemical compounds existing in the water system, such as natural organic matter (NOM), nitrite (NO_2^-), ferrous ion (Fe^{2+}) and bromide (Br^-), can enhance the NH_2Cl decay rate (Duirk et al., 2005; Vikesland et al., 2001; Zhang et al., 2017). To study the NH_2Cl dissipation in a storm sewer system, these reactions should also be considered. However, since Fe^{2+} is unstable and can easily be oxidized to ferric ion (Fe^{3+}) because of the high dissolved oxygen concentration in stormwater (Zhang et al., 2018), and the concentration of Br^- is too low to be detected by ion exchange chromatography, these two chemicals are not considered in our study.

The NH_2Cl autodecomposition model and the reactions with NO_2^- have been studied comprehensively by Vikesland et al. (2001) and Wahman and Speitel (2012). In terms of the reaction with DOM, the DOM from various water sources may have different compositions, and can show different characteristics when it reacts with NH_2Cl (Duirk et al., 2005). Therefore, to describe the NH_2Cl loss in stormwater, the principal objectives of this research are (i) to study the reactions between active chlorine species and stormwater DOM (SWDOM) during NH_2Cl dissipation processes and (ii) to develop a kinetic model to describe these processes under various stormwater conditions, such as pH, alkalinity, NH_4^+, NO_2^- and DOM concentrations. Further, our previous study showed that the NH_2Cl decay rate is largely governed by the DOM concentration in stormwater samples (Zhang et al., 2018). Therefore, the characteristics of DOM in stormwater samples collected from different neighborhoods (residential, parkland, commercial and industrial areas) were analyzed before and after chloramination.

The model developed in this research can be applied to simulate NH_2Cl dissipation rates under various stormwater conditions. The model results can be used as a reference to evaluate potential active chlorine contamination by outdoor tap water discharge, thus contributing to the regulation of outdoor chloraminated water uses, and ideally eliminating active chlorine contamination in stormwater. Since many other municipalities also use chloramines for drinking water disinfection, it is believed that the model built in this research can also benefit them. Although the SWDOM characteristics may vary among various areas, the methodology developed in this study should be widely applicable.

2. Material and methods

2.1. Experimental design

Stormwater samples collected under dry weather conditions were used for the NH_2Cl dissipation study, as relatively high TAC concentrations were detected under this weather condition during the summers of 2015 and 2016. The high TAC concentrations in stormwater are commonly caused by human outdoor tap water uses, such as landscaping and lawn irrigation from residential and park areas, car washing from commercial car dealers and realtors, and hydro-testing from industrial pressure vessel testing (Zhang et al., 2018). However, because only limited stormwater volumes can be collected from storm sewers in dry weather, the SWDOM cannot be studied by direct extraction from stormwater samples. Therefore, a commercial NOM (Nordic Reservoir NOM, purchased from International Humic Substances Society), which has a similar Fourier transform infrared (FTIR) spectrum with Edmonton SWDOM, was utilized both to study the impact of NOM on NH_2Cl dissipation, and to develop the dissipation model. A similar FTIR spectrum reflects a close chemical composition among these samples.

Laboratory DOM solutions were prepared by dissolving Nordic Reservoir NOM (NRNOM) into ultrapure water from a Barnstead™ Smart2Pure™ Water Purification System (Massachusetts, USA) to the required concentrations. NH_2Cl stock solutions were prepared with an active chlorine to nitrogen (Cl/N) molar ratio of 1.0 or 0.7 by the addition of hypochlorous acid (HOCl) and ammonium chloride (NH_4Cl) solutions into ultrapure water. HOCl and NH_4Cl standard solutions were purchased from Ricca Chemical Company (Texas, USA). Sodium bicarbonate ($NaHCO_3$) with a concentration of 4 mM was spiked into DOM solutions for pH stabilization. Hydrochloric acid (HCl) with a concentration of 6 M was added to adjust the pH to the required values. pH values from 7.0 to 8.5 were studied in this research since the stormwater pH was normally within this range (Zhang et al., 2018).

To conduct the NH_2Cl dissipation experiments in the presence of NRNOM, NH_2Cl stock solutions with an active Cl/N molar ratio of 0.7 were added into buffered DOM solutions to achieve 0.025, 0.05 and 0.1 mM of initial NH_2Cl concentrations. The concentration of 0.05 mM was selected as it is close to the NH_2Cl concentration commonly detected in tap water. Moreover, 0.025 mM and 0.1 mM were used to verify that the model can be applied under different initial NH_2Cl concentrations. Then, the solutions were transferred into 125 mL flasks wrapped with aluminum foil. NH_2Cl concentration changes were recorded at certain time intervals (1.5 h, 2.5 h, 4 h, 4 h, 12 h, 12 h, 12 h). The initial NH_2Cl concentrations were determined by adding the same amount of NH_2Cl stock solution into ultrapure water with the same volumes as the DOM solutions. Moreover, free chorine released from NH_2Cl autodecomposition can also react with DOM. In 2005, Duirk and his colleagues first indicated that rather than NH_2Cl, free chlorine is the dominant species involving in the NOM long-term reaction, and this assumption has been widely used. Therefore, in this research, the free chlorine and DOM reactions were studied with the same experimental procedure as for the NH_2Cl dissipation experiments by adding HOCl into buffered DOM solutions.

Field stormwater samples were collected from storm sewers in four neighborhoods to represent the major land-use types: (1) residential, for garden watering, (2) city parks, for lawn irrigation, (3) commercial, for car washing from dealerships and car rental businesses and (4) industrial, for pressure vessel hydro-testing. For each land use type, two stormwater samples from upstream and downstream manholes were collected. Detailed information on location selections and storm sewer distributions were described in our previous research (Zhang et al.,