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Experimental disinfection by-product formation potential following rainfall events

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ABSTRACT

Spring rainfall events can have deleterious impacts on raw and drinking water quality for water treatment plants that use surface waters. This study compares the influence of land use and climate on DBP precursors in two catchments supplying the region around the City of Québec, Canada, and assesses the variability of Disinfection By-Product (DBP) concentration and speciation following rainfall events. DBPs (trihalomethanes (THMs) and haloacetic acids (HAAs)) and their precursors in raw waters (pH, turbidity, specific ultraviolet absorbance (SUVA), total and dissolved organic carbon, bromides and chlorine dose) were monitored. Various experimental chlorination tests, DBP formation potential (DBPFP) and Simulated Distribution Systems (SDS), were also performed.

Differences in pre-rainfall (baseflow) water quality were noted according to the different watershed land uses. Raw water quality patterns showed modifications between baseflow and rainfall periods, with a degradation of raw water quality according to turbidity and SUVA in both water sources. Rainfall events were also shown to alter organic matter reactivity with an increase in THM formation potential for both sites. A less noticeable impact on HAA formation potential was observed. However, no clear differences in DBPFP tests were observed between the sites. SDS tests showed that rainfall events lead to considerable rises in organic carbon reactivity of filtered waters, even after primary treatment, with a 2-fold increase in THM and HAA concentrations following rainfall for waters representing the end of one main distribution system (20 h contact time). These increases are linked mainly to a rise in non-brominated DBPs such as chloroform, trichloroacetic acid and dichloroacetic acid. This study confirms the importance of strictly controlling OM levels during drinking water treatment to ensure safe drinking water quality throughout the distribution system.

1. Introduction

The quality of drinking water sources can decrease significantly when contaminants are transported by overland and subsurface flow and discharged into surface and ground waters following rainfall events (McCullough et al., 2012; St-Hilaire et al., 2015). Deicing salts commonly applied on roads in northeastern America may also produce saline waters that run off into the environment and pollute surface waters during rainfall (Dailey et al., 2014). Surface waters in eastern Canada (Québec, Ontario) are particularly sensitive to these types of contamination (Evans and Frick, 2001; Mayer et al., 1999).

Recent studies have suggested that changing precipitation patterns associated with climate change could have additional deleterious effects on chemical and microbiological water quality intended for human consumption by rising levels of suspended sediments, organic matter (OM), pathogens and organic contaminants in surface waters (Beaudeau et al., 2011; Delpla et al., 2009; Jiménez-Cisneros et al., 2014; Roig et al., 2011). Furthermore, increases in freeze-thaw cycles and in winter rainfall frequency associated with climate change are predicted in the Province of Québec, Canada (Des Jarlais et al., 2010). Both these phenomena could potentially lead to increasing surface water vulnerability to water pollution events during the cold season.

Recent studies have highlighted the potential impact of a changing climate on the variability of OM quality and quantity and on water treatability (Gough et al., 2015; Ritson et al., 2014). A rise in OM and contaminants in raw waters could pose a series of treatment problems such as membrane fouling and blocking, and treatment cost increases (higher chlorine demand and disinfectant

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dose, coagulant dose, pH adjustments). The rise in OM and contaminants could also impact odour, taste and colour and modify the transport of pesticides and pharmaceuticals (Ritson et al., 2014). Furthermore, an increase in OM could favour the formation of potentially harmful disinfection by-products (DBPs) during water disinfection. DBPs are an important issue in drinking water because of potential health effects, such as cancer (e.g., bladder and colorectal) and reproductive outcomes (Costet et al., 2011; Levallois et al., 2012; Richardson et al., 2007). More than 600 DBPs have been identified in water (Richardson et al., 2007). Among them, trihalomethanes (THMs) and haloacetic acids (HAAs) have been more widely studied owing to their relatively high concentrations and prevalence in drinking water.

Increasing levels of bromide in raw water could also affect DBP speciation and shift THM and HAA formation to more brominated species (Luong et al., 1982; Pourmoghaddas et al., 1993) more carcinogenic than their chlorinated analogs (Nobukawa and Sanukida, 2000; Richardson, 2003).

Several authors have stressed the fact that changes in OM characteristics occur during storm events (Hong et al., 2012; Nguyen et al., 2010, 2013). Recent studies have drawn attention to the important impact of rainfall runoff events in flushing DBP precursor compounds. The studies have highlighted the impact of storm events on dissolved OM (DOM) capability to produce THMs (Alkhatib and Peters, 2008; Delpla et al., 2015; Nguyen et al., 2013) and HAAs (Nguyen et al., 2013). They have also focused on standard formation potential tests. However, it is likely that none of the studies have compared the effects of rainfall events on different environments for different DBPs.

Some modelling attempts have been made by our team to predict DBP variation with climate and apply climate change scenarios (Cool et al., *submitted*; Delpla et al., 2016). Both studies note important differences according to season and type of treatment implemented, highlighting an increasing resilience capacity coupled with the complexity of the treatment process. However, despite an increasing number of DBP modelling studies, no Simulated Distribution System (SDS) studies have been conducted following treatment for the purpose of assessing the effects of rainfall events on drinking water quality. As a result, water managers, operators and health practitioners lack the knowledge to efficiently adapt their practices to the potential impacts of this climatic variability. It is also important to provide better information on water quality variation during the spring season when the ice cover disappears, water temperatures increase and surface waters became more vulnerable to climatic events.

The purpose of this study is to assess the impact of spring rainfall events on raw and drinking water quality in two water sources serving the region around the City of Québec, Canada, by implementing intensive monitoring campaigns and conducting experimental chlorination tests. The water sources under study are characterized by very different land-uses.

The following objectives were set for the study: i) Compare the impact of rainfall and land-use on DBP precursors and other water quality indicators in the two catchments supplying drinking water, ii) Assess the variability of DBP concentration and speciation following rainfall events during the spring season under experimental conditions for raw and simulated distributed waters.

2. Materials and methods

2.1. Study sites

The study was conducted in two catchments located in the region around the City of Québec, Canada (Saint Charles and Chaudière rivers). These catchments are characterized by different land-use types. The Saint Charles river watershed is covered mainly by forested and urban land, whereas the Chaudière river watershed is dominated by forested and agricultural land (Jobin et al., 2007). These rivers are used as source water, to produce drinking water, by two large-size treatment plants of the city of Québec and the city of Lévis (Charny). The Québec water treatment plant (WTP) provides water to almost 306 000 inhabitants using the Saint Charles River as its source water. Charny WTP uses the Chaudière River to supply water to almost 53 000 inhabitants. Treatment steps include coagulation/flocculation, sedimentation and filtration (primary treatment), followed by chlorination in both WTP. The Québec WTP uses inter-ozonation before filtration, and the Charny WTP uses inter-chlorination before filtration.

2.2. Sample collection and analysis

Twenty-four bottles refrigerated autosamplers (ISCO 6712FR) were installed at the Québec and Charny WTPs at the raw water intake at both sites. High frequency sampling campaigns were conducted for a forecasted rainfall height greater than 10 mm within 24 h. This threshold was used to define heavy rainfall (Aguilar et al., 2005; Vincent and Mékis, 2006). A total of 4 rainfall events were monitored during the 10-week study period (from April 9 to June 18, 2015). The sampling frequency was adapted to rainfall event durations in order to capture the post-rainfall effect on water quality: 1 sample/4 h for short-duration rainfall events and 1 sample/8 h for long-duration rainfall events. Then, the monitoring length for each campaign was extended from 3 to 7 days during the study, depending on the total rainfall duration.

During each sampling campaign, raw water samples were collected and transported to the laboratory every day, between 1 h and 24 h after collection. If necessary, preservation agents were added at the laboratory and the samples stored until analysis.

Conductivity was measured online (ABB probe for Québec and TBI Bailey TB701001 for Charny). pH and turbidity were measured onsite by online analyzers (Turbidity: HACH Surface scatter, pH: ABB pH probe in Québec and Rosemount Analytical Solu Comp II in Charny). Water temperature (T°) was measured online (ABB probe).

UV spectra were acquired between 200 and 400 nm with a DR5000 spectrophotometer (Scan speed: 900 nm/min, slit width: 1 nm; cell width: 5 cm). Total organic carbon (TOC) was analyzed by thermal combustion using a Shimadzu TOC-V_{CPH} analyzer. Dissolved organic carbon (DOC) was measured using the same method following filtration on previously carbonized 0.7 μm TCLP filters. Particulate organic carbon (POC) was defined as the difference between TOC and DOC. Specific ultraviolet absorbance at 254 nm (SUVA254), an indicator of the OM aromaticity (Weishaar et al., 2003), was defined as the ratio between UV absorbance at 254 nm and DOC. After filtration on 0.45 μm Whatmann filters, ammonia (NH_3) and nitrates-nitrites (NO_3-NO_2) were analyzed by colorimetry using an automated analyzer Astoria Pacific INSTR (005 or 013). Chloride (Cl^-) analysis was performed by colorimetry using an Astoria Pacific INSTR (005 or 013). Bromide (Br^-) analysis was performed by ion chromatography using method MA.303-Ions 3.2 of the Centre d'Expertise en Analyse Environnementale du Québec (CEAEQ). Since bromide analysis is costly, only three samples per campaign were analyzed, with one sample per hydroclimatic period (see next section for the definition of a hydroclimatic period). Sample selection was made on the basis of the representativeness of mean water quality for each hydroclimatic period.

THM4 (chloroform, bromodichloromethane, chlorodibromomethane and tribromomethane) were analyzed by solid phase microextraction (SPME) followed by gas chromatography analysis (Varian 3900 with a MS Varian injector 1177 and 2100T). Once the compounds were separated, they were introduced into a mass