Science of the Total Environment xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Behavior of non-regulated disinfection by-products in water following multiple chlorination points during treatment

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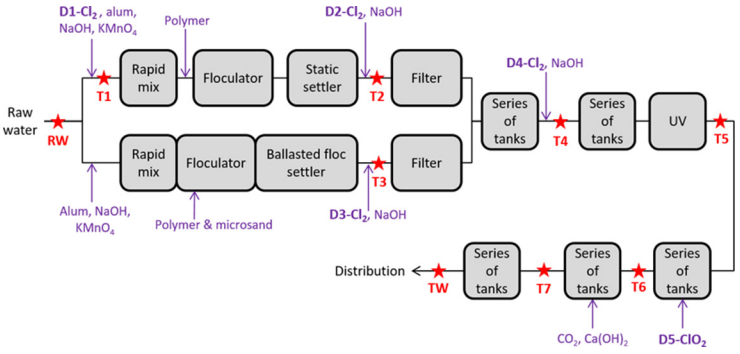
HIGHLIGHTS

- The behavior of regulated and non-regulated DBPs in drinking water is studied.
- The highest proportion of DBPs are formed within the plant and not in the network.
- The variability of DBPs is significant within the warmest period of the year.
- Specific DBP species have different behavior, some increasing other decreasing.
- Difficulties to select monitoring locations for the presence of DBPs are highlighted.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 December 2016
Received in revised form 7 February 2017
Accepted 7 February 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Disinfection by-products (DBPs)
Drinking water
Water treatment
Distribution network
Spatial variability
Monitoring strategies

ABSTRACT

In this study, the behavior of regulated (trihalomethanes–THMs, haloacetic acids–HAAs) and non-regulated (haloacetonitriles–HANs, haloketones–HKs, chloropicrin–CPK) disinfection by-products (DBPs) was investigated during treatment and distribution in a municipal drinking water system that adds chlorine at multiple points within the water treatment plant (WTP). Three to eight locations in the WTP and four locations in the distribution network were sampled weekly for DBP measurements during the warmest period of the year. The results show that most DBPs found in the study area are formed during treatment, not distribution. However, the DBP species studied behave differently during treatment and distribution. Moreover, the location where DBP concentration is the highest in the distribution network differs among species of the same family, especially HAAs and HKs, and between the sampling campaigns. As a result, the relevance of using the sum of the concentrations of the species of the same DBP family to select sampling sites for DBP monitoring is questionable. This study illustrates the difficulties that drinking water supply managers must face to control and monitor the presence of DBPs.

1. Introduction

More than 600 drinking water disinfection by-products (DBPs) have been identified so far (Richardson et al., 2007). Two families have been studied in particular and are regulated in many industrialized countries: trihalomethanes (THMs) and haloacetic acids (HAAs). Among the non-

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http://dx.doi.org/10.1016/j.scitotenv.2017.02.066
0048-9697/

regulated DBPs, some may be more harmful to human health than regulated DBPs (Richardson et al., 2007).

Various factors influence the presence of DBPs in drinking water: for example, the characteristics of the raw water source, the treatment applied and the specificities of the distribution network (Singer, 1994; Rodriguez et al., 2004; Krasner et al., 2006; Hua and Reckhow, 2008). THM and HAA concentrations are known to vary in space and time, especially in distribution networks disinfected with chlorine (Lebel et al., 1997; Weinberg et al., 2002). Some studies have examined the variability of non-regulated DBP families such as haloacetonitriles (HANs), haloketones (HKs) and halonitromethanes (HNMs) in drinking water (Lebel et al., 1997; Shin et al., 1999; Weinberg et al., 2002; Golfinopoulos and Nikolaou, 2005; Mercier Shanks et al., 2013; Guilherme and Rodriguez, 2015; Legay et al., 2015). These studies have demonstrated that these compounds evolve within the distribution network and in time, thereby making it harder to monitor them. However, these studies rarely consider the formation of non-regulated DBPs during treatment and the impact of the latter on their variability in the distribution network. Indeed, only Weinberg et al. (2002) and Golfinopoulos and Nikolaou (2005) measure the DBPs at various stages of treatment and in the distribution network. However, the number of sites sampled at the water treatment plant (WTP) or, depending on the study, in the distribution network, is relatively small. In addition, the majority of studies on DBP formation are conducted in WTP that use one or two disinfection points. Studies with WTP having multi-disinfection points are rare.

As part of the regulatory monitoring of THMs and HAAs in the USA and Canada, the parameter that represents the sum of concentrations of various species (THM4 representing the sum of four THM species and HAA5 representing the sum of five HAA species) must be below the established standard (US EPA, 2006a; Government of Quebec, 2012). For regulatory monitoring, a certain number of sites that vary according to the size of the supplied population must be sampled quarterly (US EPA, 2006a; Government of Quebec, 2012). Sampling sites must represent locations in which THM4 and HAA5 concentrations are usually the highest. Government authorities provide some guidelines to help water supply system managers choose their sampling site locations (US EPA, 2006b; DEPES, 2016).

Given that the toxicity level of species within the same family can vary (Plewa et al., 2010; Procházka et al., 2015), questions have been raised regarding the use of regulatory monitoring of a parameter representing the sum of the concentrations of many species of the same DBP family (Procházka et al., 2015). Furthermore, numerous studies have shown that certain individual HAA species may evolve differently in the distribution network (Lebel et al., 1997; Mercier Shanks et al., 2013). Consequently, the location where a species' highest concentration is measured in a network may vary from one species to the next, even within the same family.

Generally, in studies carried out on the variability of non-regulated DBPs in chlorinated drinking water (Lebel et al., 1997; Shin et al., 1999; Weinberg et al., 2002; Golfinopoulos and Nikolaou, 2005; Mercier Shanks et al., 2013; Guilherme and Rodriguez, 2015; Legay et al., 2015), the variability of individual species within the distribution network is weakly investigated and discussed. The most accurate studies show that for HAN and HK families, individual species do not behave in the same way within the distribution network (Lebel et al., 1997; Mercier Shanks et al., 2013; Guilherme and Rodriguez, 2015). However, in Lebel et al. (1997), only three sites are sampled in the distribution network and DCAN is the single HAN species for which the spatial variability is discussed. In Guilherme and Rodriguez (2015), only small distribution networks are investigated and the presence of DBPs during the treatment is not assessed. Mercier Shanks et al. (2013) average DBP concentrations measured at sampling sites with approximately the same water residence times. As a result, the specificities of each site are not considered. In most studies, the relevance of the use of a sum parameter to survey individual non-regulated DBP species within the distribution network is not really discussed.

The objective of this article is to present the behavior of two regulated DBP families and three non-regulated DBP families (HANs, HKs, HNMs) during treatment and distribution in a full-scale municipal water system that uses multiple points for disinfection. For this purpose, three to eight locations in the WTP and four locations in the distribution network were sampled weekly during the four warmest months of the year. The behavior of each DBP species in the WTP and the distribution network was investigated. Moreover, the spatial variation of the relationship between the concentrations of individual species from a same, or different, DBP family was evaluated. Strategies taking account of DBP species characteristics were discussed to select the sampling sites to survey regulated and non-regulated DBPs for regulatory or monitoring purposes. This study is based on a sampling program that would serve to generate a robust database on DBPs within the WTP and the distribution network during the hottest period of the year.

2. Methodology

2.1. Case study

The study was conducted within the WTP and the distribution network of the City of St. Jérôme (Quebec, Canada). The WTP supplies most of the City's rapidly expanding population (approximately 62,000 people). The water source supplying the WTP is the Rivière du Nord which has a watershed covering more than 2300 km^2. The treatment applied at the WTP is presented in Fig. 1. Briefly, it consists of a physical-chemical treatment (coagulation, flocculation, settling, granular filtration) operated in two parallel trains, UV disinfection, four gaseous chlorine addition points (noted D1, D2, D3, and D4) and a chlorine dioxide addition point (noted D5). Potassium permanganate is also added to raw water (0.4 to 0.5 mg/L) for taste and odor control. The coagulation conditions (alum doses and coagulation pH) are similar for the two physical-chemical trains, resulting in very similar natural organic matter (NOM) removal rates. However, the retention times are very different in these two chains: around 10–15 min for the ballasted floc settler chain and 5 h for the static settler chain. Thereafter, water residence time is estimated to be around 20 min between D2/D3 and D4, 1 h between D4 and after UV, 4 h between UV and D5 and 13 h between D5 and water distribution. The chlorine dose of 0.40 mg/L added at D1 varied approximately between 1.00 and 2.00 mg/L at D2 and D3, and between 1.00 and 2.20 mg/L at D4 (being higher at higher temperatures) during the campaigns. The chlorine dioxide dose added at D5 varied approximately between 0.25 and 0.70 mg/L. During the study, gaseous chlorine was gradually replaced by sodium hypochlorite as of the 15th sampling campaign to allow for the installation of a new chlorine dioxide generator (not installed during the study period). It is important to note that there is no re-chlorination during distribution.

2.2. Sampling strategy

For this study, 19 weekly sampling campaigns were conducted between May 29 and October 9, 2014. During each campaign, raw water (RW) and up to eight locations in the WTP were sampled (Fig. 1). Regulated DBPs were measured at all sites in the WTP, except for RW and non-regulated DBPs were measured at three sites only: T1, T4, TW. In addition, four sites located in the distribution network were sampled (Fig. 2). These sites were denoted S1 to S4 according to the ascending order of water residence time ranging from approximately 1 h (site S1) to 12 h (site S4, which represents an extremity of the network).

For each sampling site located in the distribution network, samples were taken at the restroom faucet. Cold tap water was allowed to flow for approximately 5 min to obtain water from the distribution network rather than stagnant water from the building pipes.

The DBP measurements included the analysis of regulated DBPs (THMs and HAAs) and non-regulated DBPs (HANs, HKs, HNMs). To analyze THMs and HAAs, duplicate samples were collected in 40 mL glass

Please cite this article as: Marcoux, A., et al., Behavior of non-regulated disinfection by-products in water following multiple chlorination points during treatment, Sci Total Environ (2017), http://dx.doi.org/10.1016/j.scitotenv.2017.02.066