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Disinfection byproduct regulatory compliance surrogates and bromide-associated risk

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ABSTRACT

Natural and anthropogenic factors can alter bromide concentrations in drinking water sources. Increasing source water bromide concentrations increases the formation and alters the speciation of disinfection byproducts (DBPs) formed during drinking water treatment. Brominated DBPs are more toxic than their chlorinated analogs, and thus have a greater impact on human health. However, DBPs are regulated based on the mass sum of DBPs within a given class (*e.g.*, trihalomethanes and haloacetic acids), not based on species-specific risk or extent of bromine incorporation. The regulated surrogate measures are intended to protect against not only the species they directly represent, but also against unregulated DBPs that are not routinely measured. Surrogates that do not incorporate effects of increasing bromide adequately may not capture human health risk associated with drinking water when source water bromide is elevated. The present study analyzes trihalomethanes (THMs), measured as TTHM, with varying source water bromide concentrations, and assesses its correlation with brominated THM, TTHM risk and species-specific THM concentrations and associated risk. Alternative potential surrogates are evaluated to assess their ability to capture THM risk under different source water bromide concentration conditions. The results of the present study indicate that TTHM does not adequately capture risk of the regulated species when source water bromide concentrations are elevated, and thus would also likely be an inadequate surrogate for many unregulated brominated species. Alternative surrogate measures, including THM_3 and the bromodichloromethane concentration, are more robust surrogates for species-specific THM risk at varying source water bromide concentrations.

Introduction

Disinfection is a critical step in drinking water treatment, which kills pathogenic organisms and ensures water is safe for use. However, disinfection byproducts (DBPs) form during treatment when chemical disinfectants react with natural organic matter, bromide, iodide, and other chemicals present in source waters. Since their initial discovery in the early 1970s, more than 600 DBPs have been identified in chlorinated water (Richardson et al., 2007). DBPs are of concern in drinking water because they are reported to be associated with cancer in epidemiological and animal studies (Villanueva et al., 2004, 2015; Cantor et al., 2010; Richardson et al., 1999, 2007; Bull et al., 2001). Different DBP species have different effects, with

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brominated DBPs associated with negative health outcomes at lower concentrations than their chlorinated analogs (Hrudey et al., 2015; Yang et al., 2014; Chisholm et al., 2008; Richardson et al., 2007; Echigo et al., 2004).

In response to the risk associated with use of water containing DBPs, regulations have been developed in the U.S. and other countries to limit human exposure (Australian Government, 2011; Health Canada, 2006; USEPA, 2006a, 2006b; The Council of the EU, 1998). In the U.S., DBP regulations address the occurrence of two individual byproducts (bromate and chlorite) and two common classes of DBPs (trihalomethanes (THMs) and haloacetic acids (HAAs)). DBP regulatory limits that are set based on class-sum values do not distinguish among different species within each class (which may have different risks). Although these class-sum values are considered surrogates for unregulated as well as regulated DBPs present in the water, studies have shown that they may not be adequate (Hrudey et al., 2015; Sawade et al., 2016; Bull, 2012; Weinberg et al., 2002) nor provide information about differential risk across classes (Bull et al., 2009a, 2009b). Increasing source water bromide can shift DBP speciation toward higher risk brominated species (Sohn et al., 2006) and alter class-sum value representativeness (Francis et al., 2009). Thus, changing bromide concentrations in source waters may lead to higher risk to consumers even while water continues to meet regulatory compliance requirements (Sawade et al., 2016). With more than 260 million people exposed to DBPs in drinking water (USEPA, 2005), even small changes in risk can be significant (Regli et al., 2015).

THMs and drinking water regulations

THMs, the most abundant class of DBPs formed during chlorine-based disinfection, were first reported in drinking water in 1974 (Bellar et al., 1974; Rook, 1974), and concern focused initially on the bromohaloforms as they were expected to have physiological effects greater than $CHCl_3$ (Rook, 1974). Subsequently, in 1975, the U.S. Environmental Protection Agency (EPA) conducted the National Organics Reconnaissance Survey (NORS) for Halogenated Organics in Drinking Water to measure four THM species (chloroform ($CHCl_3$), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform ($CHBr_3$)) as well as 1,2-dichloroethane and carbon tetrachloride in the treated water of 80 public drinking water utilities across the US (Symons et al., 1975). Concentrations varied widely: $CHCl_3$ (less than 0.1–311 μg/L; median = 21 μg/L); BDCM (0–116 μg/L; median = 6 μg/L); DBCM (0–100 μg/L; median = 1.2 μg/L); and $CHBr_3$ (0–92 μg/L; median = below detection).

Soon after, the National Cancer Institute published a report on the carcinogenicity of THMs (NCI, 1976), establishing precedence for the regulation of DBPs in drinking water. As a result, EPA established an interim standard, setting the allowable maximum contaminant level (MCL) at 100 μg/L for total trihalomethanes (TTHM) (USEPA, 1979). TTHM was defined as the sum of the mass-based concentrations (typically reported in μg/L) of four species: $CHCl_3$, BDCM, DBCM and $CHBr_3$.

The Stage I Disinfectants and Disinfection Byproducts (D/DBP) Rule, promulgated in 1998, lowered the MCL for TTHM from 100 to 80 μg/L and established non-enforceable maximum contaminant level goals (MCLGs) for the four THM species ($CHCl_3$ = 0 μg/L; BDCM = 0 μg/L; DBCM = 60 μg/L; $CHBr_3$ = 0 μg/L) (USEPA, 1998). The MCLGs were set to zero for the three species that were initially identified as probable human carcinogens in 1998, while DBCM was set higher at that time as data on its carcinogenicity was incomplete (USEPA, 1990). The updated MCL for TTHM was developed as a surrogate measure for excess cancer risk as a result of exposure to mixtures of DBPs through drinking water (USEPA, 2006b), with bladder cancer as the relevant outcome for the cost–benefit analysis in the regulation (Regli et al., 2015; USEPA, 2005). Additionally, Stage I included removal requirements for total organic carbon (TOC) in source water. Requiring reductions in this DBP precursor was intended to reduce DBP formation across all classes (not just THM), thus, lowering the risk associated with use of the treated water. Advanced treatment technologies used for TOC removal, such as enhanced coagulation and granular activated carbon, do not remove bromide (Krasner et al., 2016; Summers et al., 1993). The use of these advanced treatment technologies to meet TOC regulations alters the interaction of bromide and TOC in the formation of DBPs, resulting in differential formation of brominated DBPs.

To better inform the Stage II D/DBP rule and also the Long-Term 2 Enhanced Surface Water Treatment Rule (USEPA, 2006a, 2006b), EPA issued an Information Collection Rule (ICR) to collect nation-wide data (USEPA, 1996). The ICR data collection effort included the monitoring and reporting of various water quality parameters, and a variety of different DBPs, including THM, from source water, treated water, and water in the distribution system over an 18-month period (Wysock et al., 2002). The results of this national survey (McGuire et al., 2002) confirmed prior work that had identified THMs and HAAs as the dominant forms of DBPs in chlorinated drinking water (*e.g.*, Symons et al., 1975; Krasner et al., 1989; Amy et al., 1994). However, the ICR data suggested that other DBP classes (*e.g.*, haloacetonitriles, halonitromethanes) were formed in appreciable quantities. Although these non-regulated DBP classes were also correlated with THM and HAA, as observed in prior work (*e.g.*, Oliver, 1983, Krasner et al., 1989), the ICR survey led to a more in-depth study by EPA of additional non-regulated DBPs of potential concern in the 2002 U.S. Nationwide DBP Occurrence Study (Krasner et al., 2006; Weinberg et al., 2002). The two dominant classes are considered surrogates for other DBPs (Regli et al., 2015). While the use of these surrogates enabled routine monitoring and compliance evaluation (Bull, 2012; Richardson et al., 2007), some analyses question the use of TTHM as a surrogate for risk as unregulated DBPs may not be well represented by measurements of the four THMs (Hrudey et al., 2015; Sawade et al., 2016; Bull, 2012; Bull et al., 2009a, 2009b; Krasner et al., 2006; Weinberg et al., 2002), particularly when bromide is elevated (Francis et al., 2010).

In 2006, following the ICR survey and in response to the expanded epidemiological data showing human health risk from disinfected water, the Stage II D/DBP Rule updated the MCLG for $CHCl_3$ to 70 μg/L, reflecting new information that suggests that $CHCl_3$ is not a human carcinogen (Hrudey and Fawell, 2015; USEPA, 2001). The Stage II D/DBP Rule also modified compliance requirements for TTHM and HAA_5 from a running annual average (RAA) across sampling locations within the distribution system to a location-specific running annual average (LRAA) with a focus on selection of locations

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