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Review

Organic haloamines in chlorine-based disinfected water systems: A critical review

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ABSTRACT

This paper is a critical review of current knowledge of organic chloramines in water systems, including their formation, stability, toxicity, analytical methods for detection, and their impact on drinking water treatment and quality. The term organic chloramines may refer to any halogenated organic compounds measured as part of combined chlorine (the difference between the measured free and total chlorine concentrations), and may include *N*-chloramines, *N*-chloramino acids, *N*-chloraldimines and *N*-chloramides. Organic chloramines can form when dissolved organic nitrogen or dissolved organic carbon react with either free chlorine or inorganic chloramines. They are potentially harmful to humans and may exist as an intermediate for other disinfection by-products. However, little information is available on the formation or occurrence of organic chloramines in water due to a number of challenges. One of the biggest challenges for the identification and quantification of organic chloramines in water systems is the lack of appropriate analytical methods. In addition, many of the organic chloramines that form during disinfection are unstable, which results in difficulties in sampling and detection. To date research has focussed on the study of organic monochloramines. However, given that breakpoint chlorination is commonly undertaken in water treatment systems, the formation of organic dichloramines should also be considered. Organic chloramines can be formed from many different precursors and pathways. Therefore, studying the occurrence of their precursors in water systems would enable better prediction and management of their formation.

Contents

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1. Introduction

Water disinfection is a crucial step in the production of safe drinking water, whereby pathogenic microorganisms are removed or deactivated by either physical or chemical means. Some disinfection processes also provide a disinfectant residual to prevent microbial regrowth during water distribution, where the presence of a disinfectant residual is more important for large distribution systems with long retention times or when the replacement of distribution system pipes is infrequent (more than 50 years) (Rosario-Ortiz et al., 2016). Chlorination and chloramination are the most widely used disinfection practices in the world because they are effective, inexpensive, and provide disinfectant residual within the distribution system. However, while chlorine and chloramine are effective in deactivating pathogens, they also react readily with inorganic and dissolved organic matter present in the water to form unintended disinfection by-products (DBPs) (McMahen et al., 2016; Reckhow et al., 1990).

Since the discovery of DBPs in chlorinated drinking water in the early 1970s, extensive research has been undertaken to understand the formation of DBPs and their management (Richardson, 2003). While more than 600 DBPs have now been identified, minimal information on occurrence and toxicology is available for most DBPs. Furthermore, the fraction of DBPs that have been quantified in drinking water typically accounts for less than 40% of total organic halogen (Krasner et al., 2006). One group of DBPs that have not been extensively studied is nitrogenous disinfection by-products (N-DBPs). However, interest in N-DBPs has grown recently with studies showing that some N-DBPs are more genotoxic and cytotoxic than the currently regulated DBPs by several orders of magnitude (Muellner et al., 2007; Plewa et al., 2004, 2008). In particular, haloacetamides, halonitriles, heterocyclic amines and organic halamines were identified to be of highest interest from a potential toxicity perspective (Bull et al., 2011). Within these classes of DBPs, the toxicity has been reported to increase from the chlorine analogue to the bromine analogue and then to the iodine analogue, with the iodine analogue being the most toxic (Plewa et al., 2010).

Organic chloramines (more accurately referred to as organic *N*-chloramines) are compounds that contain at least one chlorine atom directly bonded to an amine nitrogen atom in an organic molecule. In the water industry, the term 'organic chloramines' typically refers to any organic halogen compounds measured as combined chlorine, the difference between the measured free and total chlorine concentration (Fig. 1). However this fraction can include a number of different chlorinated species. In this review, we refer to 'organic chloramines' as a collective term for *N*-chloramines, *N*-chloramino acids, *N*-chloraldimines and *N*-chloramides, where *N*-chloramines and *N*-chloramino acids are organic chloramines formed from amines or from amino acids, respectively. The structures and precursors of these four classes are presented in Table 1.

In this review we critically analyse the current knowledge of organic chloramines in water systems including their formation, stability and toxicity of organic chloramines, analytical methods

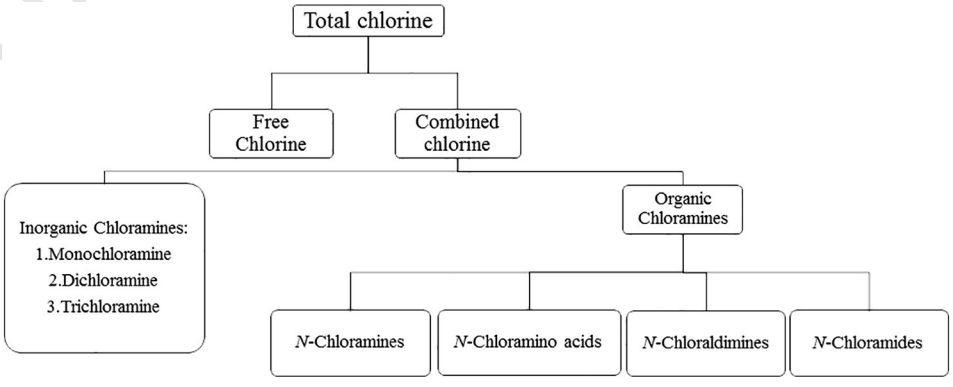

Fig. 1 – Chlorine species measured in water after chlorination or chloramination.

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