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Current trends in the analysis and identification of emerging disinfection byproducts

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ABSTRACT

Disinfection byproducts (DBPs) are a class of compounds generated during chemical disinfection processes. Their wide distribution in potable water supply systems and environmental waters has aroused concerns for both human health and aquatic organisms. Recent toxicological studies have demonstrated that most of the emerging DBPs are significantly more toxic than the regulated DBPs. Analysis techniques are prerequisites for fully understanding DBPs, as they involve identifying and quantifying DBPs, and studying their occurrence and toxicity. Accordingly, this paper reviews current trends in the analysis and identification of emerging DBPs produced in artificial water samples with model substances (e.g., natural organic matter and anthropogenic contaminants) and in real environmental waters (e.g., drinking water, wastewater effluents, swimming pool water, ballast water, cooling water from power stations, and brine reject from desalination plants).

Contents

1. Introduction

Disinfection byproducts (DBPs) are generated from reactions of natural organic matter (NOM) and inorganic ions (e.g., bromide and iodide) in source waters with disinfectants during drinking water disinfection processes, which are intended to inactivate pathogenic microorganisms and prevent outbreaks of water-borne diseases [1]. Chlorine is the most widely used and best characterized disinfectant due to its efficiency, economy of operation, and convenience [2]. But concern over potential health risks of DBPs (especially trihalomethanes (THMs)) formed from chlorination has led to the adoption of alternative disinfectants (such as chloramines, chlorine dioxide, and ozone). Yet recent studies have demonstrated that potential health risks still exist; the alternative disinfectants produce their own sets of DBPs,

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although they generate much less chlorinated DBPs than chlorine in general [3–6].

Since trichloromethane was identified as the first DBP in chlorinated potable water in 1974, about 800 compounds have been detected as DBPs [7,8]. However, only 18 of these are regulated by the US Environmental Protection Agency (EPA), European Union (EU), and World Health Organization (WHO). These DBPs are four THMs, five haloacetic acids (HAAs), chlorite, bromate, chloral hydrate, dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile, cyanogen chloride, formaldehyde, and 2,4,6-trichlorophenol. It should be mentioned that the WHO Guideline provides specific value for its each DBP, whereas the US EPA Regulation and the EU Standard use "Total THMs" to regulate the sum of the concentrations of four THMs. Unregulated DBPs are considered as emerging DBPs [9,10]. Epidemiologic studies have indicated that consumption of disinfected drinking water is related to incidences of pregnancy abnormalities, bladder cancer, colorectal cancer and other disease [1]. Although many DBPs have demonstrated mutagenic, carcinogenic, and teratogenic potential in toxicological studies, risk assessments have shown that the magnitude of health risks revealed in those studies may not be attributed to the currently regulated DBPs [11,12].

Increasing attention is being given to the emerging DBPs, as evidence from many toxicological studies has demonstrated that most of the emerging DBPs present elevated toxicity relative to the regulated DBPs. Commonly known emerging DBPs include halonitromethanes, iodo-acids, iodo-THMs, halofuranones (e.g., MX), haloamides, and nitrosamines (e.g., nitrosodimethylamine (NDMA)) [13–15]. Li's group identified a new class of DBPs called halobenzoquinones (HBQs), which induced greater adverse effects than most of the regulated DBPs in *in vitro* cytotoxicity and mutagenicity experiments [12]. Zhang's group developed precursor ion scan methods and identified dozens of new halogenated aromatic DBPs (including halohydrobenzoquinones) in chlorinated/chloraminated water samples [16–19]. A growing number of new emerging DBPs continue to be found and identified. Among these emerging DBPs, nitrogenous DBPs (N-DBPs), iodinated DBPs (I-DBPs) and brominated DBPs (Br-DBPs) are toxicologically significant [20–24]. *In vitro* mammalian toxicity tests have demonstrated that nitrogenous DBPs are considerably more cytotoxic and genotoxic than their carbonaceous DBP analogues [20,25]. Nitrogenous DBPs of interest mainly include haloamides, nitrosamines (particularly NDMA) and nitroaromatic DBPs. Br-DBPs are generally more cytotoxic, genotoxic, and carcinogenic than their chlorinated analogues, and their iodinated analogues present substantially higher toxicity than Br-DBPs [26,27].

DBPs have also been detected during chemical disinfection of waters other than drinking water, including swimming pool waters, wastewater effluents, ballast water, cooling water from power stations and brine reject from desalination plants [28–33]. It has been reported that materials originating from the human body (e.g., hair, skin, saliva, and urine) and personal care products (e.g. lotions) can react as DBP precursors with disinfectants in recreational waters, exposure to which could increase the risks of asthma and bladder cancer [34,35]. Watson et al. [36] assessed wastewater effluents' toxicity with a series of bioassays. They showed that DBPs generated from chlorinated wastewater effluents are toxic and may harm the biota of receiving water bodies. Werschkun et al. [37] reported several chlorine-substituted DBPs and Br-DBPs (with the latter predominating) produced from chlorination or ozonation of seawater and brackish water using new ballast water treatment systems for ships. The predominance of Br-DBPs, such as bromoform and dibromoacetonitrile, has also been reported in chlorinated cooling water (seawater) from power stations located on the northwestern European coast [38]. The application of chemical disinfection is essential in seawater desalination plants to prevent biofouling during pretreatment and to control pathogen contamination during post-disinfection of desalinated water. Many of the DBPs formed during pretreatment are retained in the rejected brine by reverse osmosis and pose a threat to both humans and aquatic organisms when discharged into the environment [39].

The primary focus of this review paper is to discuss current analytical methods for the detection and identification of emerging DBPs in various artificial water samples and real environmental waters. The current analytical methods consist of three major procedures: sample pretreatment, chromatographic separation, and detection. The emerging DBPs in water samples without pretreatment are usually present at concentrations below the limit of detection (LOD) of analytical instruments, and thus sample pretreatment (e.g., extraction and concentration) is essential to ensure the accuracy of measurements. As matrices of concentrated water samples are complex, chromatographic techniques are usually adopted to separate different components of the mixtures so that the target compounds can be analyzed at specific retention times with the coupled detectors. Detection forms the core of each analytical method. It aims at identifying the structure of emerging DBPs and quantifying their concentrations in different water samples.

2. Sample preparation and pretreatment

2.1. Sample preparation

Sample collection is an indispensable step for studies investigating DBP occurrence in real environmental waters. After collection, water samples were usually stored in amber glass bottles that had been cleaned with organic solvents (e.g., acetone, ethanol, and methanol) and water. Teflon containers were also used for collecting larger volumes of wastewater samples [18,19,26,33]. As bacterial activities could alter the sample characteristics, the collected samples were delivered to the laboratory in cooled boxes or ice coolers as soon as possible [18,19,26,33,40,41], and in some cases their pH values were adjusted between 2 and 3. Because suspended particles might interfere with the analysis, sample filtration was conducted in several studies, using membrane filters with pore size ranging from 0.22–11 μm [19,40].

In studies surveying DBP occurrence, because the species and concentrations of the analytes may change with time when residual disinfectants are present in collected samples, the disinfectants are often quenched immediately upon collection. Quenching agents including formic acid, ascorbic acid, ammonium chloride, sodium thiosulfate, $(NH_4)_2SO_4$ and $NaAsO_2$ have been used to remove residual chlorine in samples [16,42–45]. Malliarou et al. reported that ammonium chloride can react with hypochlorous acid to form chloramine, which inhibits the formation of THMs and HAAs, but chloraminated DBPs can still be generated after the addition of ammonium chloride [46]. A comprehensive study investigated the effects of quenching agents on the stability of DBPs, indicating that none of the quenching agents is universally suitable for all the DBPs studied; ascorbic acid and sodium sulfite are recommended for analysis of organic DBPs (e.g., THMs, HAAs and haloacetonitriles) and inorganic DBPs (e.g., bromate, chlorate and chlorite), respectively [47]. It was demonstrated that sulfite as a quenching agent caused decomposition of some organic DBPs [48]; Instead, arsenite, a weaker reductant, has been used as an alternative quenching agent [45]. It should be noted that the DBPs investigated in the study are commonly known DBPs. However, there is no comprehensive study concerning the effects of quenching agents on the stability of new emerging DBPs. Thus,