

Characterization of Natural Organic Matter and Disinfection By-products Formed after Chemical Disinfection of Water

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Abstract

The present work aims at investigating the effects of chlorine and chloramine-based disinfection processes on organic matter and the formation of disinfection byproducts (DBPs) in drinking water treatment plants (WTPs). For this, water from four water treatment plants with different characteristics in terms of the type of disinfectant used (chlorine or chloramine) and source water type (groundwater, surface water, or artificially recharged groundwater) was analysed before and after the chemical disinfection process. Specific and generic extraction approaches, and target, suspect and non-target screening approaches using advanced mass spectrometry were used and are currently being explored to characterize the different water matrices.

Keywords: drinking water treatment, chemical disinfection, non-target screening, mass spectrometry, DBP precursors, AOX

1. Introduction

Chemical disinfection of water is commonly applied to protect public health from waterborne infectious diseases. Chemical disinfectants are strong oxidants that react with the building blocks or alter the metabolism of pathogenic organisms, eventually killing them as a ultimate consequence (Russell 2003). These oxidative reactions are not substrate-specific, and thus, all organic and inorganic constituents of the water may be involved. The changes of the organic matter and the disinfection by-products (DBPs) formed are dependent on the disinfectant used, the conditions at which the disinfection reaction is conducted, and the natural organic matter (NOM) and inorganic precursors present in the water (Krasner 2009). To date, less than 50% of the halogenated material formed during chlorination and ozonation processes has been characterized (Krasner et al. 2006). Most of the DBPs known to date belong to the

semi- to high-volatile fraction of the adsorbable organic halides (AOX) formed during the disinfection processes. However, a recent study indicates that the toxicity potential of this fraction may be less relevant than that of the non-volatile fraction of the AOX, for which major constituents and characteristics are largely unknown (Stalter et al. 2016).

In this context, the present work aims at investigating the effects of chlorine and chloramine-based disinfection processes on organic matter and the formation of DBPs in drinking water treatment plants (WTPs). Furthermore, the AOX fraction will be characterized to increase the knowledge on the formation of semi-polar and non-volatile DBPs in water.

2. Material and Methods

2.1. Sample collection

Water samples (24 L) were collected in POP-cans (12 L; Sharpville container/NSF Component[®]) by grab sampling before and after the chemical disinfection process at four DWTPs in Sweden. The WTPs were selected to represent the usage of different types of disinfectants and source waters (Table 1).

Water samples were stored at 4°C in the dark until extraction, which took place in less than 48 hours of sample collection.

2.2. Sample extraction and analysis

Sample extraction for non-target and suspect screening analyses was conducted using two different methods in triplicate. In total 5 L of acidified water (pH 2.5) was concentrated onto an Atlantic HLB-H disk using an automated SPE-DEX 4790 system (Horizon Technology). The methanolic extract obtained (~30 mL) was divided for non-target analysis with ultrahigh

resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and suspect analysis with liquid chromatography-Orbitrap mass spectrometry (LC-Orbitrap MS).

The other generic-purpose extraction protocol used for water characterization consisted on the extraction of 1 L of water (pH not modified) using in-house built cartridges containing four different SPE sorbents (Strata-X, Isolute ENV+, Strata-X-AW and Strata-X-CW, from Biotage). More details of this method are provided in Gago-Ferrero et al. (2015). Extracts obtained were analyzed by means of LC-Orbitrap MS.

Liquid-liquid extraction (LLE) methods using methyl tert-butyl ether (MTBE) or ethyl-acetate were used to extract 47 target DBPs, including trihalomethanes, haloacetamides, haloacetonitriles, haloacetic acids, and haloacetaldehydes. Extracts obtained were investigated through target approaches by means of gas chromatography-mass spectrometry (GC-MS). GC-MS analysis of haloacetic acids required extract derivatization with diazomethane.

AOX, a non-target quantitative surrogate measurement of the halogenated material, was analysed according to ISO standard 9562:2004.

Table 1. Characteristics of the water and WTPs sampled

CODE	Source water	Final disinfectant	TOC (mg/L)*	Br ⁻ (mg/L)*	Residual total Cl ₂ (mg Cl ₂ /L)**
WTP1	Artificial groundwater	NaOCl	3.7	0.11	0.50
WTP2	Surface water	NH ₂ Cl	4.8	0.064	0.34
WTP3	Groundwater	NH ₂ Cl	2.5	0.21	0.24
WTP4	Surface water	NaOCl	4.0	0.052	0.13

*measured before disinfection; **measured after disinfection

3. Results

3.1. Target analysis

The highest concentrations of target DBPs were detected at WTP1 and WTP4, with 36 µg/L and 50 µg/L, respectively, which is likely caused by the use of chlorine. In contrast, the total DBP levels quantified in chloramine based WTPs (WTP2 and WTP3) were <2 µg/L.

According to the DBPs analyzed, the formation of iodine containing DBPs of the investigated waters is in general low (< 8%) (I⁻ levels in source waters were below the method limit of quantification (LOQ) of 0.025 mg/L). The DBP mixture from WTP1 presented the highest levels of bromine containing DBPs (excluding those that contained also iodine; 74% of total DBPs formed contained bromine in their structure) followed by WTP4 (39%). However, because of the high Br⁻ levels in the WTP3 source water, bromine incorporation into NOM during chloramination could also be expected, although not reflected in the target analytes.

3.2. AOX analysis

AOX concentrations were in line with the total target DBP concentrations observed in disinfected waters, with decreasing levels in the order WTP4 > WTP1 > WTP2 > WTP3. AOX data also indicate that while a large proportion of the halogenated material is explained by target DBPs analyzed in chlorinated water, the composition of the chloraminated DBP mixtures is largely unknown.

3.3. Non-target FT-ICR MS analysis

Preliminary results indicate that a wide diversity of DBPs was formed. The highest diversity of bromine and chlorine containing features identified as DBPs was observed in WTP2 and WTP4. Monohalogenated Br- and Cl-DBPs dominate the mixture in WTP3, whereas Cl- and diCl-DBPs were dominant in WTP4 disinfected water. WTP1 and WTP2 showed Br-, Cl-, and diCl-DBPs in similar proportions.

3.4 Suspect LC-Orbitrap MS analysis

Suspect analysis of the halogenated features formed during the disinfection process will be conducted by comparing the features to halogenated features contained in different libraries.

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