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Monitoring emerging chlorination by-products in drinking water using UV-absorbance and fluorescence indexes

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ABSTRACT

Recent studies have shown that emerging disinfection by-products (DBPs), such as haloacetonitriles (HANs), are much more toxic than regulated DBPs (e.g., trihalomethanes, THMs). Thus, this study explored the use of spectroscopic indexes to monitor the formation of unregulated emerging DBPs in chlorinated raw or treated water from the Ancipa Water Treatment Plant in Sicily (Italy). Specific attention was given to the formation of DBPs in treated water in order to evaluate the application of this approach for real time monitoring of DBPs in water distribution systems. In this study, it was found that total haloacetonitriles (THAN) occurs in chlorinated drinking waters at lower concentration than that of total trihalomethanes (TTHM), while total haloacetic acids (THAA) occurs at the highest concentration. Obtained results have shown that changes in UV-absorbance and fluorescence of natural organic matter (NOM) observed in chlorinated treated water are quantifiable as well as in raw waters. Very strong correlations were found between concentrations of emerging and unregulated DBPs (e.g., HANs) and UV-absorbance or fluorescence indexes. These correlations are very strong even for treated water containing very low concentrations of some DBPs species. Therefore, the examined spectroscopic indexes can be used to monitor the formation of emerging DBPs in practically important situations.

Keywords: Chlorination; Disinfection by-Products; Natural organic matter; Real time monitoring; Spectroscopy

1. Introduction

Chlorination of drinking water has been widely recognized as one of the most effective public health measures ever. However, chlorination has some drawbacks such as the low efficiency in the deactivation of some pathogens (e.g., Giardia and Cryptosporidium) and the formation of disinfection by-products (DBPs) that are generated from the reaction of chlorine with natural organic matter (NOM) present in all surface waters [1].

Organic DBPs include several chlorinated, brominated and iodinated species that are grouped in distinct classes [2]. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the classes of DBPs generally present at the highest levels (ppb) in chlorinated water, with chloroform generally being the dominant THM and dichloroacetic acid and trichloroacetic acid being the dominant HAAs [3]. Although more than 500 DBPs have been reported in the literature [4], more than 50% of the total organic halide (TOX) formed during the chlorination of drinking water are unknown [5].

In order to control DBPs in drinking water systems, the use of alternative disinfectants, such as ozone, chlorine dioxide, ultraviolet (UV) radiation and chloramines, has been pursued, leading to reduction of some regulated DBPs. However, other emerging DBPs are generated in these conditions [5–6] and bacterial regrowth may occur using physical disinfection techniques such as UV

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radiation and advanced oxidation processes (AOPs) [7]. As a result, chlorine is still the most used disinfectant, especially for secondary disinfection, because its cost and stability that help maintain a residual in water distribution systems.

Among emerging DBPs, several species occur at much lower concentrations than those of regulated DBPs but their toxicities are higher [3,5]. For instance, it was found that N-containing DBPs are more toxic than C-containing DBPs [3,8]. The nature of halogen atoms incorporated in DBPs also affects their toxicity which follows an I>> Br >> Cl order [3].

DBPs formation is strongly affected by the type and dose of disinfectant, content and reactivity of the organic precursor (NOM), concentrations of inorganic precursors (bromide and iodide), pH, temperature and reaction time. However, mechanisms of DBPs formation in disinfected water are not fully understood, because the complexity of both NOM and the halogenation process [6,9,10].

Several models have been developed in order to understand how water quality parameters affect DBPs formation, to explore the kinetics of DBPs formation or to predict DBPs yields in the field [11]. Modeling DBPs consists of establishing relationships between DBPs levels in waters and the parameters of water quality that can be linked to their formation. Several studies have focused on the effects of chlorine dose and NOM characteristics, with particular interest to the reactivity sites. Other water quality parameters, such as pH, water temperature, bromides, chlorine dose and reaction time of residual chlorine, are also often taken into account [11]. Fundamentally, models for DBPs formation have been developed using statistical and limited mechanistic approaches.

Alternative approaches based on differential absorbance or fluorescence have been also developed [12–14]. However due to variety of individual DBP species, site-specificity of NOM, and pronounced effects of water chemistry parameters on DBP formation and speciation, development of a model that would take into account all these aspects is extremely challenging.

The objective of this study is to investigate the performance of developed spectroscopic indexes in monitoring the formation of emerging unregulated DBPs in chlorinated raw and treated waters. Specific attention was given to the formation of DBPs in treated water in order to evaluate the application of this approach for real time monitoring of DBPs in water distribution systems.

2. Materials and methods

2.1. Water used

Experiments were carried out using water samples from the inlet and outlet of the water treatment plant (WTP) that treats the water from Ancipa reservoir (also named Lake Sartori). Ancipa reservoir has a capacity of 20 million of cubic metres and is used mainly for water supply.

The Ancipa WTP is projected to treat about 1,000 l/s and is a conventional WTP that includes coagulation, flocculation and sedimentation, intermediate chlorination and sand filtration. Samples from the inlet (denoted as "Ancipa raw") and the outlet (denoted as "Ancipa treated") of Ancipa WTP were used. The DOC concentration in Ancipa raw water was 2.9 mg/l, $SUVA_{254}$ was 2.8 $l\ mg^{-1}\cdot m^{-1}$ and pH 7.9. On the other hand, the DOC in Ancipa Outlet sample was 2.0 mg/l and $SUVA_{254}$ was 1.8 $l\ mg^{-1}\cdot m^{-1}$.

All chemicals were of ACS reagent grade or better. Solvents used in extractions were of high-purity grade. Reagent water was obtained from a Millipore Super-Q Plus water system. Chlorine stock solution was prepared by dilution of a reagent grade sodium hypochlorite solution (5% available chlorine) with Milli-Q water.

2.2. Experimental methods

Chlorination experiments with Ancipa water were conducted in the dark at 20°C in 1.6 l PTFE sampling bags. The samples were chlorinated with sodium hypochlorite at pH 7.0 in the presence of 0.03 mol/l phosphate buffer. Initial chlorine doses were 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 mg Cl_2 per mg DOC. Reaction times ranged from 10 min. to 3 d. Chlorinated samples were quenched with requisite amounts of Na_2SO_3 or NH_4Cl and stored at 4°C for no more than 10 d before being analysed for DBPs concentrations.

2.3. Analytical methods

Chlorine concentrations were determined using the standard *N*,*N*-diethyl-*p*-phenyldiamine (DPD) colorimetric method [15]. UV absorbance spectra were measured using a 5 cm quartz cell on a Perkin-Elmer Lambda 18 spectrophotometer. All spectra were normalized to a 1 cm cell length. Fluorescence spectra (with excitation at 320 nm) were obtained with a Perkin-Elmer LS-50B fluorometer. TOC was analyzed using an O.I. Analytical 1010 total organic carbon analyzer. Concentrations of THMs, HANs and HAAs were determined using standard analytical procedures (EPA methods 551.1 and 552.2) and a Perkin-Elmer AutoSystem gas chromatograph equipped with an electron capture detector. Other aspects of these analyses are described in previous publications [13,14,16].

3. Results and discussion

3.1. Formation kinetics of major DBPs in chlorinated Ancipa treated water

As observed in previous studies [13,16], concentrations of all major stable DBP species increased monotonically

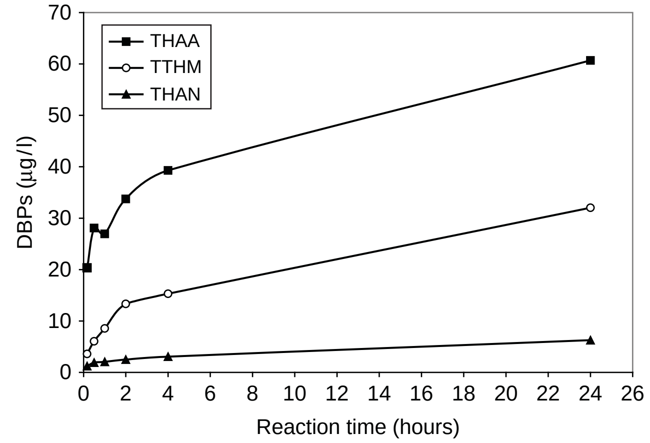

Fig. 1. Kinetics of formation of TTHM and THAA and THAN in chlorinated Ancipa treated water at chlorine to DOC ratio of 0.75.

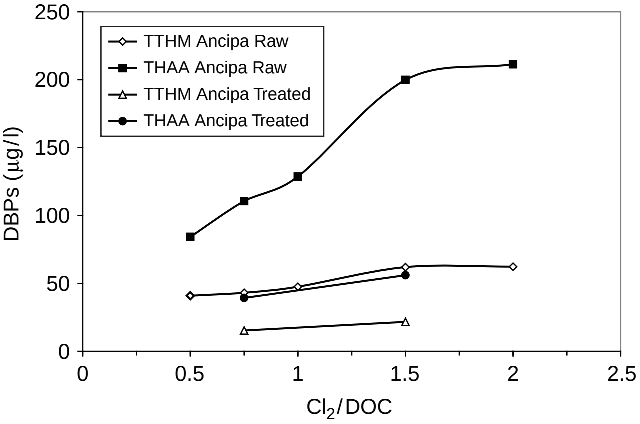

Fig. 2. Yields of TTHM and THAA in Ancipa raw and treated waters at 4 h of reaction time and different chlorine doses.

either with time or chlorine dose. For example, Fig. 1 shows the kinetics of total THMs (sum of chloroform, dichlorobromomethane, bromodichloromethane and bromoform, TTHM), total HAAs (sum of monochloroacetic acid, monobromoacetic acid, chlorobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid, tribromoacetic acid, dichlorobromoacetic acid and dibromochloroacetic acid, THAA) and total HANs (sum of dichloroacetonitrile, trichloroacetonitrile, bromochloroacetonitrile and dibromoacetonitrile, THAN) formation in chlorinated Ancipa treated water. Obtained results highlight that HANs are present in Ancipa chlorinated treated waters but at much lower concentration than of THMs and HAAs.

The halogenation of NOM present in chlorinated Ancipa treated water and release of THMs, HAAs and HANs was relatively rapid. At chlorine doses higher than 1 mg per mg of DOC, THAA concentrations reached 44–50% of their maximum levels observed for a 3 d reaction period within 2 to 4 h of chlorination. Comparable yields of TTHM (33–49%) and THAN (30–39%) were observed in the same conditions.

In accord with previous studies on DBP formation [17–19], THAA concentrations were consistently higher (more than 2 times) than those of TTHM, especially at higher chlorine doses (Fig. 2). As observed in Fig. 2, this conclusion can be carried out either for chlorinated Ancipa raw or treated waters. This result supports the concept that HAAs may need to be regulated in Mediterranean countries as well as in Europe.

As reported in Fig. 2, examination of dependence of DBPs yields vs. chlorine to DOC ratios showed that chlorine dose has a strong impact on the ratio between THAA and TTHM concentrations, especially at chlorine to DOC ratio higher than 1.0. This result highlights the need to determine a chlorine dose threshold to control the formation of HAAs.

Although the concentrations of THAN were found always lower than those of TTHM or THAA, due to the higher toxicity of nitrogenous DBPs the control of this class of DBPs should be pursued and therefore the use of surrogate parameter to monitor their formation may be very useful. This aspect is explored in the next sections.

3.2. *Changes in UV-absorbance and fluorescence spectra observed during NOM chlorination*

Similarly to results observed for different surface raw waters [e.g., 13,16,20], the differential absorbance spectra of chlorinated Ancipa treated water, defined as $\Delta A_\lambda(t) = A_\lambda(t) - A_\lambda(t = 0)$, had a prominent peak near 272 nm and their intensity increased with increasing reaction time, as shown in Fig. 3.

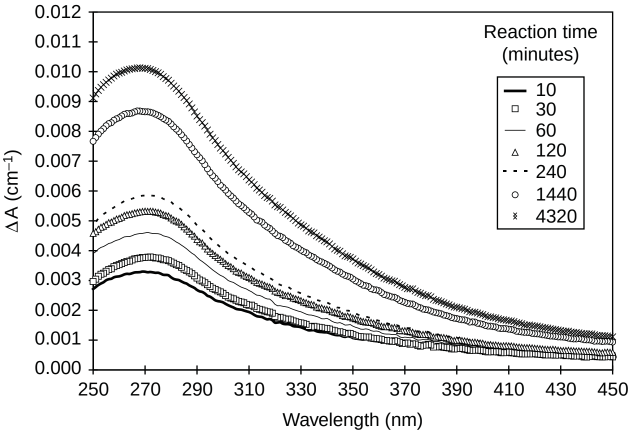

Fig. 3. Differential absorbance spectra obtained for chlorinated Ancipa treated water at varying reaction time and chlorine to DOC ratio 1.5.

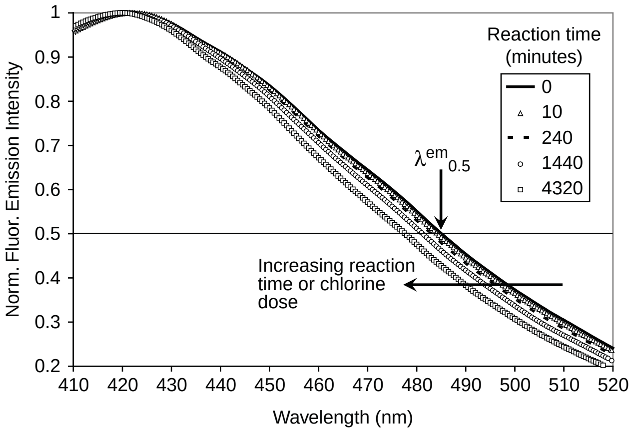

Fig. 4. Normalized fluorescence spectra obtained for chlorinated Ancipa treated water at varying reaction time, and chlorine to DOC ratio 1.5.

The intensity of fluorescence emission spectra of chlorinated Ancipa treated water was non-monotonic. However, as observed in prior research for different surface raw waters [14,21], the position of the normalized emission band at its half-intensity (for wavelengths > λ_{max}), denoted as $\lambda_{0.5}^{em}$, exhibited a blue shift that became increasingly prominent at higher reaction times, as demonstrated in Fig. 4. To quantify the changes in NOM fluorescence two indexes were calculated. They are the differential position of wavelength that corresponds to 50% of the maximum intensity of fluorescence and differential ratio of fluorescence emission intensities measured at 500 and 450 nm defined as $\Delta\lambda_{0.5}(t) = \lambda_{0.5}(t) - \lambda_{0.5}(t = 0)$ and $\Delta(I_{500}/I_{450}) = (I_{500}/I_{450})(t) - (I_{500}/I_{450})(t = 0)$, respectively [14].

3.3. Correlations between concentrations of emerging DBPs and spectroscopic indexes for chlorinated Ancipa treated water

Very strong correlations were found between differential absorbance values and the concentrations of emerging and unregulated DBPs species obtained from the chlorination of Ancipa waters. For example, Fig. 5 shows the relationship between the concentration of THAA and differential absorbance index for chlorinated Ancipa treated water. These correlations are valid regardless of chlorine doses, reaction time and temperature, in accord to prior research that has shown similar correlations for TTHM and THAN [13].

In agreement to results observed in previous studies [14,21], also some selected fluorescence indexes were found strongly correlated with the concentration of several groups of DBPs. In particular, in this study very strong correlations were found between the concentrations of emerging DBPs (e.g., HANs) and, on the other hand, $\Delta\lambda_{0.5}^{em}$ or $\Delta(I_{500}/I_{450})$ indexes. For example, Fig. 6 shows the relationship between the concentration of THAN and $\Delta\lambda_{0.5}^{em}$ values for chlorinated Ancipa treated water. $\Delta(I_{500}/I_{450})$ index was found to perform as well as $\Delta\lambda_{0.5}^{em}$, resulting in similar correlations with different DBPs species.

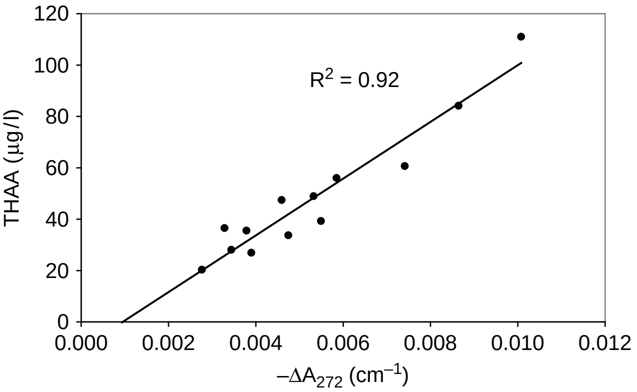

Fig. 5. Correlations between the concentration of THAA and ΔA_{272} values for chlorinated Ancipa treated water at chlorine to DOC ratio from 0.75 to 1.5 and reaction time from 10 min to 3 d.

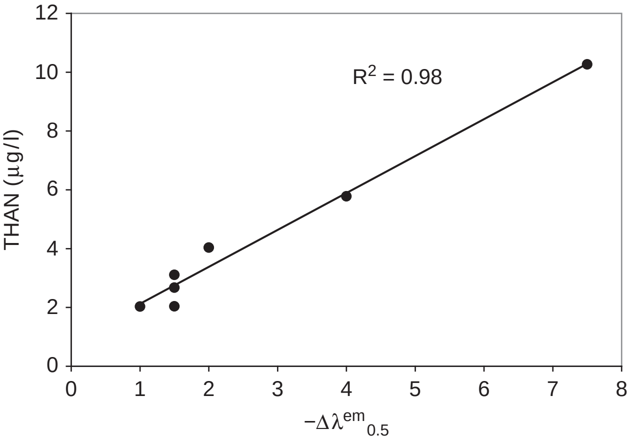

Fig. 6. Correlations between the concentration of THAN and $\Delta\lambda_{0.5}^{em}$ values for chlorinated Ancipa treated water at chlorine to DOC ratio of 1.5 and reaction time from 10 min to 3 d.

Overall, obtained results highlight that the selected spectroscopic indexes that were strongly correlated with the concentrations of individual or groups of DBPs in chlorinated raw waters [13,14] may be used also to predict and control the concentrations of emerging DBPs species (e.g., HANs) present at trace levels in treated waters.

4. Conclusions

Results generated in this study confirm that THAN often occurs in chlorinated drinking waters at lower concentration than that of TTHM, while THAA may occur at the highest concentration. Therefore, due to the occurrence of THAA at higher level and to the higher toxicity of THAN, the formation of these emerging or unregulated DBPs should be controlled in drinking water systems.

In this study, very strong correlations were found between concentrations of THAA or THAN and, on the other hand, absorbance or fluorescence based indexes. These correlations are very strong even for treated water that contains very low concentrations of HANs. Therefore, the examined spectroscopic indexes can be used to control the formation of emerging DBPs in practically important situations. In particular, the application of differential absorbance and/or fluorescence spectroscopy may allow real time monitoring of emerging DBPs species in water distribution systems.

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