

# Quantifying the formation of nitrogen-containing disinfection by-products in chlorinated water using absorbance and fluorescence indexes

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## ABSTRACT

Among known but unregulated disinfection by-products (DBPs), several nitrogenous species (N-DBPs) have been found in drinking waters. While concentrations of N-DBP are much lower than those of trihalomethanes (THMs) and haloacetic acids (HAAs), their potential toxicity is higher. In this study the relationships between the formation of N-DBPs and the changes in NOM caused by the chlorination of raw Ancipa water quantified by the use of differential absorbance and fluorescence indexes were investigated. Very strong relationships were found between selected N-DBPs (i.e. trichloronitromethane and dichloroacetonitrile) and the proposed spectroscopic indexes that were previously developed to quantify the changes in natural organic matter (NOM) during chlorination at varying reaction conditions (chlorine dose, reaction time and temperature) and the generation of DBPs. Obtained results clearly indicate that the changes in NOM absorbance and fluorescence are fundamental descriptors of the formation of both commonly controlled halogenated DBPs and N-DBPs. This approach may be suitable for real time monitoring of emerging N-DBPs and for studying their formation pathways.

**Key words** | absorbance, fluorescence, haloacetonitriles, halonitromethanes, monitoring.

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## INTRODUCTION

Since the discovery of disinfection by-products (DBPs) formed as result of halogenation of natural organic matter (NOM) and the toxicity problems related to them (Rook 1974), extensive efforts have been carried out to determine their identities and toxicity, to model their formation and control their occurrence (Krasner *et al.* 2006; Richardson *et al.* 2007). Many countries have issued specific regulations for controlling some individual and/or groups of DBPs. Limit values have been set for trihalomethanes worldwide while haloacetic acids are the second group of DBPs regulated in accord with many drinking water standards. While these two groups of DBPs have been regulated based on their occurrence and toxicity, more than 500 DBPs have been reported in the literature (Richardson 1998) and more than 50% of the total organic halides (TOX) formed during the chlorination of drinking water (Krasner *et al.* 2006) are not identified.

Among known but unregulated disinfection by-products (DBPs), several species have been found in drinking waters at

lower concentrations than those of trihalomethanes (THMs) and haloacetic acids (HAAs) but their potential toxicity is higher (Krasner *et al.* 2006; Richardson *et al.* 2007). For instance, the Nationwide Occurrence Study of unregulated priority DBPs carried out in USA determined a wide occurrence of several nitrogenous DBPs (N-DBPs). Among these N-DBPs, haloacetonitriles (HANs) and halonitromethanes (HNMs) have received special attention because they are ubiquitous in drinking waters and toxic (Krasner *et al.* 2006; Richardson *et al.* 2007). Indeed, recent studies have determined that cyto- and genotoxicity of the nitrogenous DBPs are much more prominent than those of carbonaceous DBPs (Plewa *et al.* 2004, 2008; Muellner *et al.* 2007).

Due to the complexity of both NOM per se and halogenation processes, several surrogates (TOC, DOC, UV absorbance indexes) have been used to quantify NOM reactivity in DBPs formation. Among those parameters, absorbance of ultraviolet light at 254 nm ( $A_{254}$ ) and its specific value

( $SUVA_{254}$ ), which is the ratio between  $A_{254}$  and DOC, are probably the most widely used (Croué *et al.* 2000; Kitis *et al.* 2001, 2002). An alternative approach based on the use of differential absorbance and fluorescence indexes have been developed that was useful to track the halogenation of NOM and generation of DBPs and to better understand the mechanism of DBPs formation (Korshin *et al.* 1999, 2002; Roccaro *et al.* 2008; Roccaro & Vagliasindi 2009). Time-specific differential absorbance was found a very good surrogate to quantify the reactivity of NOM in THMs and HAAs formation (Roccaro *et al.* 2009). Although these studies have investigated the relationships between several DBPs species and spectroscopic indexes, these relationships have not been fully investigated for N-DBPs. Therefore, the objective of this study was to examine these relationships for Haloacetonitriles (HANs) and Halonitromethanes (HNMs) in chlorinated raw surface water during the halogenation process at varying reaction conditions. In particular, this paper is focused on dichloroacetonitrile (DCAN) and trichloronitromethane (chloropicrin, CPN) because they are the N-DBPs (HANs and HNMs, respectively) that occurs at higher concentrations in chlorinated waters.

## MATERIALS AND METHODS

### Water source used and experimental methods

Water source used in this study was raw water from the Ancipa reservoir (Sicily, Italy). The DOC and  $SUVA_{254}$  of the sample used in this study were  $2.9 \text{ mg L}^{-1}$  and  $2.89 \text{ L mg}^{-1} \text{ m}^{-1}$ , respectively. Chlorination experiments were conducted in the dark at varying chlorine dose (0.25 to 2.00 mg of chlorine per mg of DOC), reaction time (10 minutes to 7 days) and temperature (3 to 34°C). The sample was first filtered at  $0.45 \mu\text{m}$  and then was chlorinated with sodium hypochlorite at pH 7.0 with the presence of  $0.03 \text{ mol L}^{-1}$  of phosphate buffer. In each case the chlorinated samples collected were analyzed only if chlorine residual was found. When necessary, sodium sulfite or ammonium chloride was used to quench the residual chlorine. Chlorinated samples were refrigerated at 4°C for no more than 10 days before to be analyzed for DBPs concentrations.

### Analytical methods

Chlorine concentrations were determined using the standard DPD colorimetric method. UV absorbance was analyzed using a 5 cm quartz cell on a Perkin-Elmer Lambda 18 UV/Vis

Spectrophotometer at  $\lambda = 200\text{--}600 \text{ nm}$ . 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, other volatile and semi-volatile DBPs (including HANs and HNMs) 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 and experimental procedures are described in previous publications (Korshin *et al.* 1999, 2002; Roccaro *et al.* 2008, 2009).

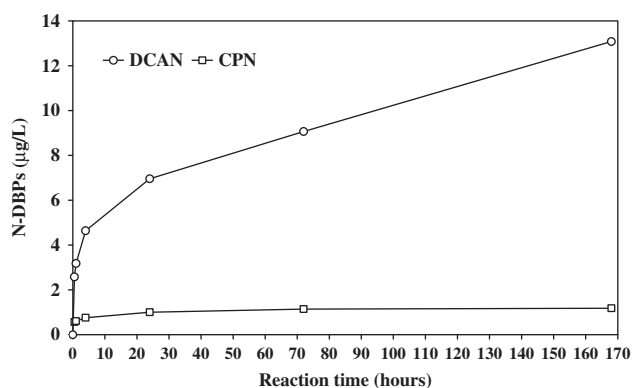
## RESULTS AND DISCUSSION

### Formation of N-DBP in chlorinated Ancipa water

In agreement with previous studies (Reckhow *et al.* 1990; Croué *et al.* 2000; Kitis *et al.* 2002), concentrations of all major stable DBP species increased monotonically either with time or chlorine dose. DCAN concentrations in Ancipa chlorinated water were higher than those of other HANs and increased monotonically with reaction time as shown in Figure 1 for the chlorination experiment carried out at chlorine to DOC ratio of 2 mg per mg and at 20°C. Also CPN showed a similar behaviour with a monotonic increase of its concentration with reaction time or chlorine dose (Figure 1). However, a significant difference in the concentrations of DCAN and CPN was found as reported in Figure 1. Indeed, the concentrations of CPN were about an order of magnitude less than those of DCAN. Overall, comparison of the kinetics of N-DBPs formation and those of regulated carbonaceous DBPs (C-DBPs) (Figure 1 and Figure 2) shows that the concentrations of N-DBPs tended to be at least an order of magnitude less than C-DBPs. These differences in the formation of N-DBPs versus C-DBPs are in agreement with the data of previous studies (Krasner *et al.* 2006; Richardson *et al.* 2007; Lee *et al.* 2007; Hu *et al.* 2010a, 2010b).

### Relationships between N-DBP concentrations and spectroscopic indexes

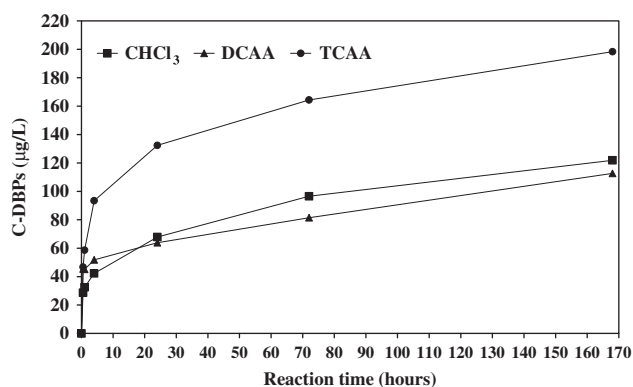
Our previous publications (Korshin *et al.* 1999, 2002; Roccaro *et al.* 2008, 2009) have demonstrated that there is a strong correlation between the formation of individual DBPs or their groups and, on the other hand, the changes in NOM caused



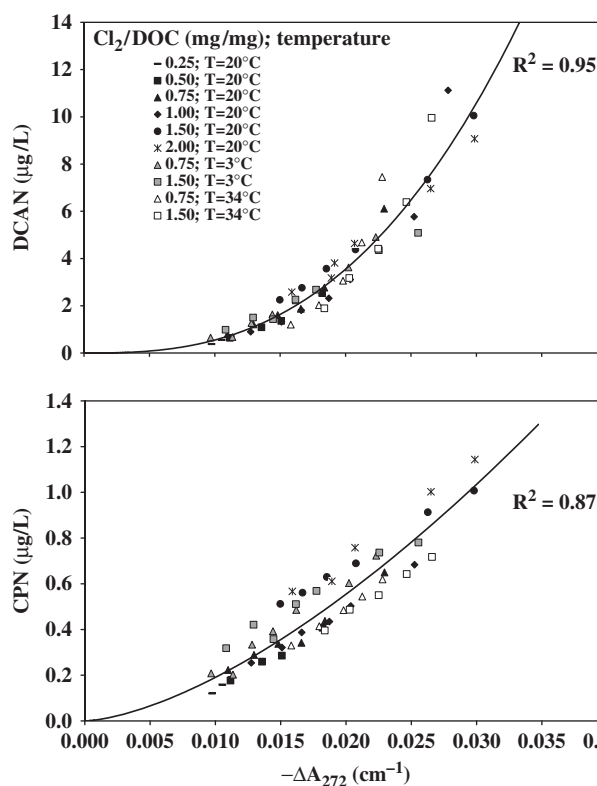
**Figure 1** | Kinetics of dichloroacetonitrile (DCAN) and trichloronitromethane (CPN) formation at chlorine to DOC ratio of 2.00 mg/mg in chlorinated Ancipa raw water at 20°C.

by the chlorination of raw and treated waters. These changes have been quantified by the use of differential absorbance at 272 nm, defined as  $\Delta A_{272}(t) = A_{272}(t=0) - A_{272}(t)$ , or two differential fluorescence that were calculated as  $\Delta \lambda^{em}_{0.5}(t) = \lambda^{em}_{0.5}(t=0) - \lambda^{em}_{0.5}(t)$  and as  $\Delta(I_{500}/I_{450})(t) = I_{500}/I_{450}(t=0) - I_{500}/I_{450}(t)$ .

The correlations between DBPs concentrations and these spectroscopic indexes were observed for several C-DBPs and to some extent also for N-DBPs (Korshin et al. 2002; Roccaro et al. 2008, 2009). These results are reinforced by the results obtained in this study that have found similar strong correlations for other emerging N-DBPs (e.g. DCAN and CPN) regardless of the reaction conditions (varying chlorine dose, reaction time and temperature). For instance, Figure 3 shows the correlations between  $\Delta A_{272}$  values and, on the other hand, DCAN and CPN concentrations, while Figure 4 shows the correlations for  $\Delta(I_{500}/I_{450})$  obtained with the same reaction conditions. Similar correlations were found also for  $\Delta \lambda^{em}_{0.5}$ .



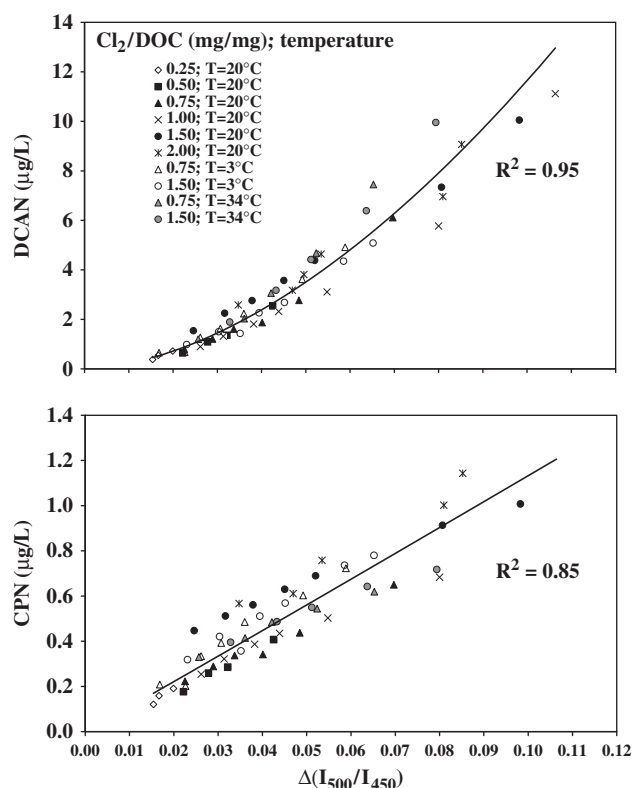
**Figure 2** | Kinetics of chloroform ( $\text{CHCl}_3$ ), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) formation at chlorine to DOC ratio of 2.00 mg/mg in chlorinated Ancipa raw water at 20°C.



**Figure 3** | Correlations between selected N-DBPs (DCAN and CPN) and differential absorbance at 272 nm at varying chlorine to DOC ratio (from 0.25 to 2.00), reaction time (from 10 minutes to 7 days) and temperature (from 3 to 34°C) in chlorinated Ancipa raw water.

In our previous publications, we have shown that differential absorbance quantifies with high precision changes of NOM aromaticity caused by the incorporation of halogens in the predominantly aromatic attack sites of NOM,  $\Delta \lambda^{em}_{0.5}$  quantifies the shift of the entire NOM emission band of fluorescence, while the  $\Delta(I_{500}/I_{450})$  track the contraction of the NOM emission band. Both fluorescence indexes can be considered as indicators of the destruction of the reactive aromatic groups in NOM and breakdown of NOM molecules accompanied by the release of DBPs (Korshin et al. 1999; Roccaro et al. 2009).

Previous studies on the formation of N-DBPs have reported that organic nitrogen moieties of dissolved organic carbon (DOM) are precursors for DCAN upon chlorination (Reckhow et al. 1990; Lee et al. 2007). Furthermore, the dissolved organic nitrogen (DON) may act as an indicator of several N-DBPs formation potential (e.g. DCAN, CPN and dichloroacetamide (DCAcAm)) but it is not a predictor per se of these DBPs (Chu et al. 2010; Hu et al. 2010a). It has been reported that several N-DBPs occur at higher yields in treated waters, due to a limited removal of their precursors during conventional water treatment processes, but no good



**Figure 4** | Correlations between selected N-DBPs (DCAN and CPN) and differential ratio of fluorescence intensities at 500 and 450 nm at varying chlorine to DOC ratio (from 0.25 to 2.00), reaction time (from 10 minutes to 7 days) and temperature (from 3 to 34°C) in chlorinated Ancipa raw water.

correlations were found between DON or DOC/DON and most N-DBPs (Chu *et al.* 2010; Hu *et al.* 2010a), with the exception of DCAN that was correlated with DOC/DON to some extent (Reckhow *et al.* 1990; Lee *et al.* 2007). Among the organic nitrogen precursors of N-DBPs, amino acids have been suggested to play a major role (Trehy *et al.* 1986; Chu *et al.* 2010; Hu *et al.* 2010a). In particular, specific amino acids that possess reactive groups such as amino nitrogen, sulphur or activated aromatic rings were found to have a major role in chlorine consumption and TOX formation observed in the case of the chlorination of polypeptides (Hureiki *et al.* 1994). Furthermore, Chu *et al.* (2010) have shown that the amino acids that formed DCACAm during chlorination were similar to those that generated DCAN in a previous study (Ueno *et al.* 1996) and four of these amino acids have aromatic rings as part of their R-groups (i.e. histidine, phenylalanine, tyrosine and tryptophan).

These findings agree with the very strong correlation found between DCACAm yields and  $\Delta\text{SUVA}_{254}$  values obtained by the chlorination of different NOM fractions (Chu *et al.* 2010). This highlights the point that the formation

of these N-DBPs is intrinsically correlated with the destruction of the aromaticity of the DOM. Overall, the results obtained by independent research groups reinforce the interpretation of results obtained in this study that show strong correlations between N-DBPs concentrations and alternative absorbance or fluorescence indexes that may quantify the destruction of the reactive aromatic groups in NOM and breakdown of NOM molecules accompanied by the release of DBPs.

While the complex mechanism of NOM halogenation and ensuing release of DBPs remain to be completely understood, the strong relationships found between C-DBPs or N-DBPs concentrations and the spectroscopic indexes employed in this study clearly indicate that the changes in NOM absorbance and fluorescence are mechanistically associated to the formation of organic-halogenated DBPs and may be suitable for controlling emerging N-DBPs formation and for understanding DBPs formation pathways.

## CONCLUSIONS

This study establishes that trihalonitromethane (CPN) and dichloroacetonitrile (DCAN) occur in chlorinated Ancipa raw water at concentrations two and one order of magnitude less than of carbonaceous DBPs (C-DBPs), respectively. The formation of these two nitrogenous DBPs (N-DBPs) is highly important because their toxicity is significantly higher than that of C-DBPs.

Very strong relationships were found to exist between concentrations of CPN and DCAN and, on the other hand, spectroscopic indexes based on absorbance and fluorescence measurements, namely  $\Delta A_{272}$ ,  $\Delta(I_{500}/I_{450})$  and  $\Delta\lambda^{\text{em}}_{0.5}$ , developed to quantify the changes of the properties of natural organic matter (NOM) during chlorination at varying reaction conditions (chlorine dose, reaction time and temperature).

Since the developed spectroscopic indexes ( $\Delta A_{272}$ ,  $\Delta(I_{500}/I_{450})$  and  $\Delta\lambda^{\text{em}}_{0.5}$ ) are indicators of the degradation of the reactive aromatic groups in NOM and breakdown of NOM molecules accompanied by the release of DBPs, it is likely that the formation of N-DBP is associated to the chlorination of activated aromatic groups in NOM. This speculation is corroborated by the results obtained by other research groups that have reported that major N-DBPs precursors are amino acids and N-containing heterocyclic aromatic rings. Thus, results of this study clearly indicate that the changes in NOM absorbance and fluorescence are fundamental descriptors of the formation of organic-halogenated

N-DBPs and may be suitable for real time monitoring of emerging N-DBPs and for studying of formation pathways of emerging DBPs.

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