From Micropollutant to DBP Driver: The Unexpected Reactivity of 1-Chlorobenzotriazole in Water Disinfection

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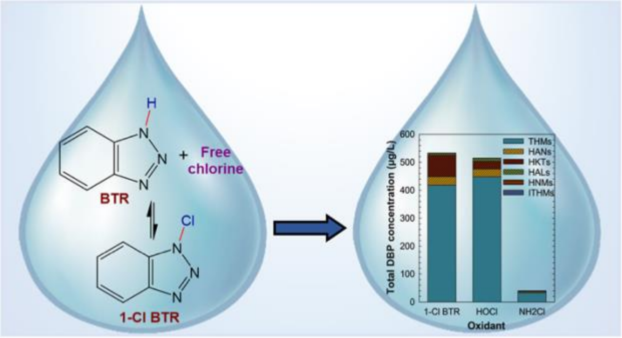
ABSTRACT

The increasing adoption of potable wastewater reuse is challenged by persistent micropollutants—such as benzotriazole—which are poorly removed by conventional treatment and may produce toxic disinfection by-products(DBPs). This study investigated benzotriazole chlorination and identified 1-chlorobenzotriazole as the primary product, formed preferentially under near-neutral to acidic pH and excess chlorine—conditions typical in disinfected water. The DBP formation potential of 1-chlorobenzotriazole was evaluated using two organic matter standards, and secondary wastewater effluents, and compared against chlorine and monochloramine. Surprisingly, 1-chlorobenzotriazole formed DBP levels comparable or greater than those from chlorine, including trihalomethanes, haloaldehydes, haloketones, haloacetonitriles, and halonitromethanes. This reactivity is attributed to 1-chlorobenzotriazole's ability to function as a free chlorine reservoir, sustaining chlorination reactions and promoting continued DBP formation—unlike inorganic *N*-halamines. DBP speciation was strongly pH-dependent and mirrored chlorine behavior, supporting the chlorine reservoir effect. Additionally, 1-chlorobenzotriazole exhibited precursor- and matrix-dependent reactivity, especially with complex matrices like secondary wastewater effluents, where it acted both as a chlorine source and direct DBP precursor. Overall this work provides the first detailed evaluation of 1-chlorobenzotriazole DBP formation potential, revealing an overlooked pathway for halogenated DBP production in water disinfection and emphasizes the importance of considering benzotriazole transformation products in advanced reuse systems.

Keywords: Disinfection byproducts, *N*-halamines, water treatment, benzotriazole, formation mechanism, chlorination

Synopsis: 1-chlorobenzotriazole was identified as a major chlorination product of benzotriazole, that acts as a free chlorine reservoir and mimics free chlorine reactivity.

Graphical Abstract



INTRODUCTION

Potable wastewater reuse is increasing in many countries, yet the incomplete removal of micropollutants during treatment remains a critical concern.[1,2] Micropollutants—including pharmaceuticals, per- and polyfluorinated alkyl substances (PFAS), flame retardants, pesticides, hormones, and benzotriazole (BTR)—are frequently detected in treated wastewater effluents, posing risks to aquatic ecosystems and human health.[3-6] Chemical disinfectants can react with micropollutants to form transformation products that may exhibit enhanced toxicity and higher reactivity relative to their parent compounds.[5,7-9] While disinfectant by-product (DBP) formation from pharmaceuticals has been reported,[9] and PFAS have been shown to promote DBP production in drinking water pipes,[10] information on BTR as a halamine and DBP precursor remains limited.[11]

BTR is an inexpensive, odorless, and stable synthetic compound widely used as a component in corrosion inhibitors, UV stabilizers, aircraft de-icing fluids, and household detergents.[12-15] BTR has high water solubility (28 g L^{-1}), low vapor pressure, low octanol-water partition coefficient (log K_{ow}=1.23), and is resistant to biodegradation, which contribute to its persistence in the environment.[16,17] For this reason, BTR has been detected in wastewater effluents,[18,19] surface water,[16,20,21] groundwater,[22,23] drinking water,[24-26] and human urine.[27,28] Loos *et al.* reported BTR concentrations between 2.1 to 221 μg/L in 90 wastewater effluents across Europe, with a detection frequency of 97%.[18] The elevated BTR concentrations reported in wastewater effluents highlight the limited removal efficiency of conventional wastewater treatment processes, allowing BTR to enter drinking water sources, where an average concentration of 30.9 ng/L has been reported in 80 tap water samples collected from southeast England.[24]

BTR is a heterocyclic compound composed of a fused benzene and triazole ring, which can undergo electrophilic substitution on the benzene ring and on the nitrogen atoms of the triazole ring.[14] BTR has been reported to react with sodium hypochlorite (NaOCl) in aqueous acetic acid to produce 1-chlorobenzotriazole via substitution at the N1 position.[29] 1-chlorobenzotriazole—reported as a strong oxidant in synthetic chemistry[29-31]—may facilitate reactions with organic matter to potentially form disinfection byproducts (DBPs).[29] Recent studies investigated the degradation kinetics of BTR under UV/chlorine or sunlight/chlorine processes and found that reactive chlorine species are responsible for BTR degradation.[32,33] Yang *et al.* proposed mono- and di-benzene ring substituted chlorinated BTR products only—not 1-chlorobenzotriazole—and identified chloroform as the major product out of seven DBPs studied.[32] However, studies from the Lin group observed high levels of 1-chlorobenzotriazole[33] and bromoform as a major DBP in the presence of bromide.[34] Despite these advances, 1-chlorobenzotriazole's role on DBP formation remains unclear.

The objectives of this study were to (1) assess if 1-chlorobenzotriazole is a major product of BTR chlorination and (2) determine its DBP formation potential with two organic matter standards—Suwanee River humic acid (SRHA), Suwanee River natural organic matter (SRNOM)—and secondary wastewater effluents (SWE), and directly compare it with chlorine (HOCl), and monochloramine (NH_2Cl) DBP formation potential. This study aims to elucidate the role of 1-chlorobenzotriazole on DBP formation and provide critical insights to assess and mitigate emerging risks in potable wastewater reuse systems.

EXPERIMENTAL SECTION

Chemicals and reagents

All standards were obtained at the highest available purity levels and detailed in Text S1 in the Supporting Information (SI). 1-chlorobenzotriazole reference standard was analyzed with ^1H NMR before DBP formation experiments to confirm structure and purity as shown in Figure S1 in the SI. SRNOM and SRHA were purchased from the International Humic Substances Society (St. Paul, MN, USA). SRNOM and SRHA were chosen because they were identified as major DBP precursors compared to Suwanee River fulvic acid due to the high abundance and diversity of reactive amino compounds.[35]

Chlorine demand free water (CDFW) was prepared following Standard Method 4500-Cl C,[36] and chlorine demand free glassware was prepared as described elsewhere.[37] DBP reference standard solutions were prepared as described elsewhere (Text S2 in the SI).[38]

Sampling location and water quality parameters

SWE were collected from the secondary clarifier at Advancing Canadian Water Assets (ACWA), a full-scale water treatment research facility, in November 2024. Samples were stored at 4 °C in 4 L amber glass bottles with no headspace to minimize exposure to atmospheric contaminants. Water quality parameters, as detailed in Table S2 in the SI, were analyzed by ACWA and the Kimura-Hara lab described in Text S3 in the SI.

BTR chlorination and sample analysis

All reaction samples were prepared with CDFW. Reagent-grade NaOCl was standardized before use via UV-Vis spectrophotometry at 292 nm (molar absorptivity = 350 M^{-1} cm^{-1}).[39,40] BTR chlorination reactions were conducted at pH 5.5 and 7.5 with 10 mM phosphate buffer ([BTR]=0.1 mM), and at pH 9.5with 10 mM carbonate buffer ([BTR]=0.05 mM). Three Cl_2/BTR molar ratios (10:1, 1:1, and 0.5:1) were evaluated at each pH condition, maintaining a final reaction volume of 100 mL. All reactions were stirred at 400 rpm in 125 mL amber borosilicate bottles covered with aluminum foil and sealed with PTFE-lined polyethylene caps. Aliquots were collected at 0.5 min, 6, 12, and 24 h, and immediately analyzed using a UV-Vis spectrophotometer (model UV-2700, Shimadzu Corp., Japan) from 200-400 nm in 1 nm increments. Control experiments were performed with CDFW, BTR, and HOCl.

A modified liquid-liquid extraction (LLE) method based on published protocols was used to extract a BTR control sample and 24 h reaction samples for ultra high pressure liquid chromatography (UHPLC)-tandem mass spectrometry (MS/MS) analysis,[41-43] as summarized in Text S4 in the SI. An ACQUITY H-class system equipped with a Xevo TQ-S micro MS/MS fitted with a Z-spray (dual orthogonal sampling) interface (Waters Corp., Milford, MA, USA) was used for analysis. Both positive and negative electrospray ionization modes were tested to maximize the ionization efficiency of molecular ions of both BTR and chlorinated BTR standards (1-chlorobenzotriazole, 5-chlorobenzotriazole, 7-chlorobenzotriazole) prepared in a 1:1 acetonitrile/water solution at concentrations of 80–120 μg/L. The optimized MS operation parameters are summarized in Table S3 in the SI. Chlorinated BTR standards and reaction extracts were directly infused to the MS to develop multiple reaction monitoring (MRM) methods and to monitor ion fragmentation at increasing collision energy. Chlorinated BTR products were identified through LC separation in MRM mode using a modified gradient elution method,[44,45] as described in Text S5 and Table S4-S5 in the SI.

DBP formation potential and DBP quantification

Solutions of 2 mg/L as C of either SRNOM or SRHA prepared in CDFW were reacted separately with 50 μM (3.55 mg/L as Cl_2) of HOCl, 1-chlorobenzotriazole, or NH_2Cl, in headspace-free, 40 mL amber glass bottles. Reaction mixtures were buffered at pH 7.5 with 10 mM potassium phosphate buffer. NH_2Cl was prepared as described elsewhere by mixing NaOCl and NH_4Cl in 1:1 ratio.[39,46] SWE was filtered through 0.4-micron Whatman glass microfiber filter and reacted with 200 μM (14.2 mg/L as Cl_2) of either HOCl, 1-chlorobenzotriazole, or NH_2Cl. The oxidant concentration was 200 μM in the SWE experiments to compensate for the substantially higher organic carbon content of SWE (9.6 mg/L as C; Table S2). SRHA, SRNOM, SWE, and 1-chlorobenzotriazole were analyzed individually as controls. Additional controls were conducted of either SRHA or SRNOM with 50 μM BTR, and SWE with 200 μM BTR. Reaction samples in headspace-free amber bottles were incubated at 25 °C and analyzed at 24, 48 h, and 5 days for 1) free chlorine and combined chlorine using a colorimetric method[36] and 2) DBPs in triplicate using LLE followed by gas chromatography (GC)-MS/MS as described elsewhere.[38] 1-chlorobenzotriazole DBP formation potential at different pH conditions was evaluated by reacting 2 mg/L as C solutions of SRNOM with 50 μM 1-chlorobenzotriazole at pH 3.5, 5.5, 7.5, and 9.5, using 10 mM phosphate or carbonate buffers to maintain pH. At 3, 24, and 48 h time points, samples were extracted and analyzed immediately.

Extracted samples were quantified in an Agilent 7890B with a multi-mode inlet coupled to a 7000C Agilent triple quadrupole (Agilent Technologies, Santa Clara, CA) with an electron ionization source. A modified MRM method to quantify 6 DBP classes (25 DBPs in total), including haloacetonitriles, halonitromethanes, haloacetaldehydes, iodinated-trihalomethanes, trihalomethanes and haloketones, was used in this study (Table S1 in the SI).[38]

RESULTS AND DISCUSSION

Identification of *N*-halamine 1-chlorobenzotriazole

UV Experiments. Reactions between BTR and HOCl for three Cl_2/BTR ratios (1:1, 10:1, and 0.5:1) and three pH conditions (pH 5.5, 7.5, and 9.5) were monitored using a UV-Vis spectrophotometer (Figures 1 and S2-S3 in the SI). In general, results for all ratios at pH 5.5 and 7.5 showed that BTR and HOCl quickly reacted by the time the first sample was taken (30 s) with no significant degradation of the product. Two peaks (~260 and ~280 nm) were observed at the 10:1 ratio (Figure 1a-b) and slightly less at the 1:1 and 0.5:1 ratios (Figure S2a-b and S3a-b), suggesting that excess HOCl promotes the formation of a possible product. In contrast, at pH 9.5 (Figure 1c), one single peak at 274 nm was observed, where the reaction spectra was not significantly different from the sum of the individual HOCl and BTR controls. Similar results were observed for the two other molar ratios (Figure S2c-S3c), which indicate that OCl^- does not form a product with BTR. The observed findings align with previous studies that reported two absorption maxima for BTR due to the coexistence of its 1H- and 2H-tautomeric forms (Figure 2I) under acidic and neutral conditions, each contributing distinct π–π* electronic transitions.[47] At basic pH, where BTR (pKa_2 = 8.2) is fully deprotonated and exists predominantly as a single resonance-stabilized quinoid structure (anion) as shown in Figure 2II, only one absorption maximum was observed at λ ~274 nm.[45,47] Additional UV-Vis experiments were conducted comparing commercial standards with reactions; however, results were inconclusive (data not shown).[48] Therefore, the identities and structures were analyzed using UHPLC-MS/MS.

Mass spectrometry experiments. Electrophilic aromatic substitution reactions, which are known to occur on the benzene ring of BTR, may produce multiple chlorinated derivatives during chlorination.[32] This complexity poses a significant challenge in accurately identifying the structures of the chlorinated products, particularly the exact position of the chlorine attachment within the BTR rings. To address this, a MRM method was developed to analyze reaction samples by targeting transitions unique to reference standards of BTR and its chlorinated derivatives, including BTR, 1-chlorobenzotriazole, 5-chlorobenzotriazole, and 7-chlorobenzotriazole (Table S5 and Text S6 in the SI).

Reaction products were evaluated from experiments conducted at pH 5.5, 7.5, and 9.5, under three different Cl_2/BTR molar ratios each: 10:1, 1:1, and 0.5:1 (Figures S4, S5, and S6 in the SI). At molar ratio 10:1 at all three pH conditions, two distinct chlorinated products were identified at retention times (RTs) of 3.30 and 3.53 min (Figure S4a, S5a, and S6a in the SI). In contrast, at molar ratios of 1:1 and 0.5:1, only the parent compound, BTR, was detected at all pH conditions (Figures S4b-c, S5b-c, S6b-c), indicating no or trace-level formation under these conditions. Furthermore, the area counts of peaks with RTs of 3.30 and 3.53 min showed a clear trend of increasing intensity with decreasing pH (Figure S7 in the SI). The observations were consistent with the UV-Vis analysis, which indicated enhanced formation of chlorinated products in the presence of excess HOCl and particularly under acidic conditions.

To identify the two peaks, LC chromatograms of individual reference standards were compared to reaction sample Cl_2/BTR=10:1 and pH=7.5 (Figure S8 in the SI). The RTs of BTR, 7-chlorobenzotriazole, and 5-chlorobenzotriazole were determined to be 2.43, 3.24, and 3.52 min, respectively (Figure S7a-c in the SI). However, the chromatogram of the 1-chlorobenzotriazole (Figure S8d in the SI) displayed two distinct peaks with RTs of 3.26 and 3.52 min, which overlap with the RTs of 5-chlorobenzotriazole and 7-chlorobenzotriazole, making it difficult to identify reaction product(s) (Figure S8e in the SI). The two peaks by 1-chlorobenzotriazole is consistent with other studies and is attributed to possible isomerization or conformational differences.[33,49] Note that RTs from the reaction products from Figure S7 and S8 in the SI differ slightly possibly because reactions were conducted months apart and could have resulted in a slight variation in RT.

To resolve this issue, further analysis was conducted by directly infusing reaction samples and reference standards into the MS/MS to compare the fragment ions' abundance at increasing collision energy. Due to a lower bond dissociation energy, the N–Cl bond would require less collision energy to cleave this bond compared to the C-Cl bond, leading to a distinct relative abundance distribution (or fragmentation pattern) of chlorinated nitrogen-containing intermediates.[50] Each reference standard exhibited a unique relative abundance distribution of fragment ions of molecular ion *m/z* 154 with increasing collision energy (Figure 3a–c). Molecular ion (*m/z* 154) of 7-chlorobenzotriazole and 5-chlorobenzotriazole retained 100% relative abundance at 15 eV, whereas in 1-chlorobenzotriazole, the relative abundance dropped to approximately 50% at the same collision energy. The reaction extract (Cl_2/BTR = 10:1, pH = 7.5) had a similar relative abundance distribution to the 1-chlorobenzotriazole reference standard (Figure 3c-d), confirming that 1-chlorobenzotriazole is the primary chlorinated reaction product. A proposed 1-chlorobenzotriazole formation mechanism under neutral pH conditions is shown in Figure 2III. A ring nitrogen acts as a nucleophile and attacks electrophilic chlorine in HOCl to form the N–Cl bond. A subsequent proton transfer to hydroxide ion yields the neutral 1-chlorobenzotriazole product, stabilized by resonance within the triazole ring.

DBP Formation Potential Induced by 1-chlorobenzotriazole, HOCl, and NH_2Cl

In this study, we investigated the DBP formation potential of 1-chlorobenzotriazole and compared it to HOCl and NH_2Cl— two common water disinfectants. Each oxidant was reacted with two organic matter standards (SRHA, SRNOM) and a SWE sample, and monitored for 5 days. Results are summarized in Figure 4, shown by DBP class in Figures S9-S14, and presented by DBP in Tables S6-S8 in the SI. The DBP speciation profiles and concentrations from 1-chlorobenzotriazole reaction with SRHA (180-275 µg/L), SRNOM (145-225 µg/L), and SWE (530-810 µg/L) were similar to those observed from HOCl reaction with SRHA, SRNOM, and SWE—140-170, 125-175, and 510-880 µg/L, respectively (Figures 4a-b, 4d-e, and 4g-h). Results indicate that 1-chlorobenzotriazole—an organic halamine—surprisingly yields elevated DBP levels compared to NH_2Cl, an inorganic halamine. Additionally, residual free chlorine and combined chlorine levels in HOCl and 1-chlorobenzotriazole reactions were also similar which indicates 1-chlorobenzotriazole's ability to mimic free chlorine.

Trihalomethanes (THMs). THMs were the predominant DBP chemical class (>70% for NH_2Cl, and >90% for both HOCl, and 1-chlorobenzotriazole) across all precursor sources evaluated in this study (Figure 4), with the highest levels observed in 1-chlorobenzotriazole-treated SRHA samples (272 µg/L), compared to SRNOM samples (208 µg/L). The observed differences in THM formation may be attributed to compositional differences between SRHA and SRNOM. THM precursors are primarily the hydrophobic fractions of NOM, including humic acids, aromatic proteins, phenolic substances, and soluble microbial products.[51] SRHA is a well-characterized fraction of NOM, composed mainly of larger, more aromatic, and hydrophobic organic molecules with functional groups such as phenols, carboxylic acids, and aromatic rings. In contrast, SRNOM is a more complex and heterogeneous mixture, including humic acids, fulvic acids, and non-humic substances (i.e., proteins, carbohydrates, lipids) resulting in a lower hydrophobic and aromatic content than SRHA alone.[51-53] Additionally, residual free chlorine concentrations measured after 24 h were slightly lower in SRHA samples than in SRNOM samples (Figure 4), suggesting higher reactivity of both HOCl and 1-chlorobenzotriazole with SRHA, thereby enhancing THM formation.

In 1-chlorobenzotriazole-treated samples, THM concentrations were 20–50 µg/L higher than those treated with HOCl for both SRHA and SRNOM (Figure 4). In contrast, for SWE, 1-chlorobenzotriazole produced 25–50 µg/L lower THM levels than HOCl, particularly within the first 48 h. Furthermore, free chlorine concentrations in 1-chlorobenzotriazole-treated SRHA and SRNOM samples were 2.82-7.04 **µ**M (0.2-0.5 mg/L as Cl_2), lower than HOCl-treated samples, whereas the opposite trend was observed in SWE, further supporting the observed trends. The observed differences in DBP formation may be attributed to the dual functionality of 1-chlorobenzotriazole, which acts both a free chlorine reservoir and a precursor-dependent oxidant, as discussed in the subsequent section on 1-chlorobenzotriazole chemistry. The reaction between organic molecules and disinfectant/oxidant continues over time providing both are present, leading to a gradual THM formation.[51] As a weaker oxidant, NH_2Cl generated lower THM levels, consistent with previous studies.[54,55]

THMs were below the method's detection limit (MDL) in blank SRHA and SRNOM samples. However, the blank SWE sample had ~10 µg/L THMs (Figure S9 in the SI). BTR controls with either SRHA, SRNOM, and SWE had THM concentrations of 4-8, 3-11, 10-12 µg/L, respectively over 5 days, most likely from the BTR standard and the SWE sample.

Haloacetaldehydes (HALs). HALs were the second most abundant DBP class (~5-10%) with both HOCl and 1-chlorobenzotriazole across all three precursors (Figures 4). In general, SRHA produced higher HAL concentrations than SRNOM with both disinfectants, which is consistent with the reported higher HAL formation from hydrophobic fractions compared to the hydrophilic fraction.[56] HOCl can react sequentially with organic compounds, resulting in halogenation and/or oxidation to more stable byproducts. HALs and THMs represent relatively stable endpoints, whereas intermediates such as HANs and HKTs often undergo further transformation, contributing to HAL accumulation.[54] In SRHA, HAL concentrations after 5 days were slightly higher with HOCl (17.5 µg/L) than with 1-chlorobenzotriazole (10.6 µg/L), while the opposite trend was observed in SRNOM and SWE. SWE generated substantial HAL levels—especially trichloroacetaldehyde (Figure S10 in the SI). Treatment of SWE with HOCl resulted in a sharp increase in HAL concentration over 5 days (109.7 µg/L), compared to 35 µg/L with 1-chlorobenzotriazole, further highlighting the precursor-dependent reactivity of 1-chlorobenzotriazole.

Haloketones (HKTs). HKTs decreased over time across all three organic precursors with both HOCl and 1-chlorobenzotriazole (Figure 4). HKTs—along with HANs—are susceptible to hydrolysis and reactions with residual HOCl, resulting in their degradation or transformation.[54,55,57] After 24 h, both HOCl and 1-chlorobenzotriazole produced higher HKT concentrations with SRHA, SRNOM and SWE (1.5-2.1, 2.2-3.5, and 30-80 µg/L respectively) than NH_2Cl (1-1.5 µg/L); however, by day 5, HKT levels (~1 µg/L) were comparable across all disinfectants. Notably, higher concentrations of 1,1-dichloropropanone and lower concentrations of 1,1,1-

trichloropropanone and 1,1,3,3-tetrachloropropanone were observed in monochloraminated SRHA and SRNOM samples compared to those treated with HOCl and 1-chlorobenzotriazole (Figure S11d-e in the SI). In general, HOCl generates higher concentrations of HKTs than NH_2Cl, with the exception of 1,1-dichloropropanone.[54,55] Previous studies suggest that 1,1-dichloropropanone undergoes oxidation by HOCl to form 1,1,1-trichloropropanone, which subsequently hydrolyzes to produce trichloromethane.[54,55] The relatively high levels of 1,1-dichloropropanone and absence of further chlorinated HKTs in NH_2Cl-treated samples are consistent with the lower oxidative strength of monochloramine, which may limit the formation of tri- and tetra-substituted HKTs.

Unlike other DBP families, HKT formation patterns differed across the three source water precursors. In SRNOM and SRHA, 1,3-dichloropropanone and 1,1,3,3-tetrachloropropanone levels were notably higher with HOCl (0.3-0.9 µg/L) than with 1-chlorobenzotriazole (0.1-0.2 µg/L) (Figure S11d-e in the SI**)**, suggesting that 1-chlorobenzotriazole contributed minimally to the formation of higher chlorine-substituted HKTs. Furthermore, concentrations of 1,3-dichloropropanone, 1,1,3,3-tetrachloropropanone, and 1,1-dichloropropanone were approximately twice as high in SRNOM (~0.38-0.9 µg/L with HOCl) compared to SRHA (~0.2-0.45 µg/L with HOCl), indicating that SRNOM facilitated HKT formation more effectively (Figure S11d-e in the SI**).** This trend may be attributed to the broader range of smaller, more reactive organic compounds in SRNOM (i.e, alcohols, aldehydes, and ketones), which are more susceptible to chlorination. In contrast, SRHA—despite serving as a major precursor for other chlorinated DBPs such as THMs—may contribute less to HKT formation due to its large, hydrophobic, polymeric structure.

In SWE, the complex matrix had a pronounced influence on both the formation and degradation of HKTs over time, with formation patterns under 1-chlorobenzotriazole and HOCl treatment differing substantially from those observed for other DBP classes. After 24 h, 1,1-dichloropropanone (32.2 µg/L) and 1,3-dichloropropanone (36.3 µg/L) levels were higher in 1-chlorobenzotriazole-treated SWE compared to HOCl-treated SWE (9.6 and 7.5 µg/L, respectively; Figure S11f in the SI). This suggests that intermediate species formed in 1-chlorobenzotriazole-treated SWE were insufficient to further oxidize/degrade di-substituted HKTs to stable DBPs (i.e., THMs) within the 24 h reaction period. Conversely, the low 1,1-dichloropropanone levels and elevated THM concentrations observed in HOCl-treated SWE (Figures S11f and S9c in the SI) indicate a more rapid transformation of 1,1-dichloropropanone to trichloromethane, likely via 1,1,1-trichloropropanone. Additionally, the lower 1,1,3,3-tetrachloropropanone levels produced in 1-chlorobenzotriazole-treated samples compared to those treated with HOCl (Figure S11f in the SI) indicate that 1-chlorobenzotriazole does not readily promote further chlorination of di- and tri-substituted HKTs, consistent with observations in SRHA and SRNOM.

Haloacetonitriles (HANs) and halonitromethanes (HNMs). Two N-DBP families, HANs and HNMs, were also analyzed. SWE produced higher levels of N-DBPs compared to SRHA and SRNOM (Figure 4a-b,d-e). Combined chlorine concentrations were negligible in HOCl and 1-chlorobenzotriazole-treated SRHA and SRNOM samples, indicating the absence of chloramines in these matrices. In contrast, combined chlorine concentrations remained at approximately ~11.3 µM (~0.8 mg/L as Cl_2) in SWE samples treated with HOCl and 1-chlorobenzotriazole over the 5-day period (Figure 4g-h), suggesting chloramine formation, likely from the reaction of free chlorine with nitrogen-containing species (Table S2). Low nitrogen-content in SRHA and SRNOM (~1% w/w)[58] likely accounts for the limited N-DBP formation.

HAN concentrations in both 1-chlorobenzotriazole- and HOCl-treated SRHA and SRNOM samples were ~2.5 μg/L within 24 h but generally decreased over time, likely due to degradation or transformation to other DBPs (Figure S12a-b in the SI). In contrast, HAN levels in NH_2Cl-treated samples increased over 5-day period, likely because NH_2Cl serves as a nitrogen precursor for HANs and HNMs.[59] HANs are typically formed via two main pathways: (1) the amine pathway and (2) the aldehyde pathway, in which NH_2Cl plays a key role.[39,46,60,61] Therefore, the observed accumulation of HANs over time in NH_2Cl treatments is likely driven by its weak yet persistent reactivity through the aldehyde pathway, which promotes HAN formation. Dichloroacetonitrile was the predominant HAN with concentrations of ~2.4 μg/L in SRHA and SRNOM, and ~25 μg/L in SWE for both HOCl and 1-chlorobenzotriazole treatments (Figure S12d-f in the SI). This aligns with literature reports indicating that dichloroacetonitrile is more stable and consistently observed at higher concentrations than other HANs.[62,63]

Unlike SRHA and SRNOM, SWE produced multiple HAN species, including trichloroacetonitrile, dichloroacetonitrile, chloroacetonitrile, bromoacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile (Figure S12f in the SI). The presence of bromide (50 μg/L) in SWE (Table S2 in the SI) accounts for the formation of brominated HANs (Br-HANs), which are reported to be more toxic than their chlorinated analogs.[64] HOCl and 1-chlorobenzotriazole treatments produced similar HAN profiles in SWE, with concentrations between 25–32 μg/L and a slight increase over 5 days. In contrast, NH_2Cl treatments resulted in lower HAN levels, increasing from ~4 to ~8 μg/L, with no detectable bromoacetonitrile or dibromoacetonitrile (Figures S12c, f in the SI). According to literature, chlorination of organic precursors—such as amino acids—in the presence of bromide leads to the formation of organic bromamine intermediates, which react faster than their chlorinated counterparts, accelerating Br-HAN formation.[65] In NH_2Cl treatments, however, Br-HAN formation is suppressed due to the preferential formation of inorganic over organic bromamine intermediates.[65] This likely explains the high Br-HAN levels observed with HOCl and the lower levels with NH_2Cl. Br-HAN concentration in 1-chlorobenzotriazole-treated samples were similar to those from HOCl treatments, highlighting 1-chlorobenzotriazole's ability to mimic free chlorine.

In this study, we quantified only one HNM species, dichloronitromethane. Dichloronitromethane concentrations in SRHA and SRNOM were less than 0.2 μg/L for all three oxidants (Figure S13 in the SI). In SWE, NH_2Cl produced the highest dichloronitromethane concentration (1.21 μg/L) after 5 days, while HOCl and 1-chlorobenzotriazole resulted in concentrations below 1 μg/L. The elevated dichloronitromethane levels with NH_2Cl are likely attributable to its role as an additional nitrogen source.[60,66] However, due to the stable molecular structure of BTR, the extent to which 1-chlorobenzotriazole contributes nitrogen to dichloronitromethane formation remains uncertain.

Iodinated-trihalomethanes (ITHMs). ITHMs are commonly used as indicators to examine iodinated DBP (I-DBPs) formation potential.[67] In this study, we observed only dichloroiodomethane which was absent in SRHA and SRNOM samples but were present at notable concentration levels in SWE, with NH_2Cl producing the highest dichloroiodomethane concentration (0.49 μg/L) after 5 days (Figure S14 in the SI). The complex composition of SWE may contain a variety of organic and inorganic constituents, including trace amounts of iodide (I^-), which although not detected in this study (MDL < 1 μg/L),[68,69] can account for the low but detectable dichloroiodomethane levels (<1 μg/L). Although both NH_2Cl and HOCl can oxidize I^- to hypoiodous acid (HOI), where iodine is in the +1 oxidation state, HOCl rapidly oxidizes HOI to iodate, a non-toxic and stable end product.[70] In contrast, NH_2Cl oxidizes HOI more slowly, allowing more time for HOI to react with organic nucleophiles and form I-DBPs,[67,71] as observed in this study. Additionally, 1-chlorobenzotriazole produced slightly higher dichloroiodomethane concentrations than HOCl (Figure S14 in the SI), suggesting a higher potential to stabilize HOI and promote I-DBP formation—similar to NH_2Cl.

pH Effect on DBP formation. The DBP formation potential from the reaction of 1-chlorobenzotriazole and SRNOM was assessed across different pH conditions (3.5, 5.5, 7.5, and 9.5). We hypothesized that 1-chlorobenzotriazole would exhibit DBP speciation trends similar to those observed with HOCl. UV–visible spectra of SRNOM showed minimal changes in absorbance across the tested pH values (Figure S15 in the SI), suggesting negligible structural changes in SRNOM. Therefore, variations in DBP formation were attributed primarily to pH-dependent changes in the speciation and reactivity of 1-chlorobenzotriazole (Figure 5, Table S9 in the SI). 1-chlorobenzotriazole produced the highest THM concentrations at pH 9.5 (188 μg/L) and the lowest at pH 3.5 (66.2 μg/L) after 48 h. This trend aligns with previous studies reporting increased THM formation with increasing pH during HOCl disinfection.[54,55,72-74] In contrast, concentrations of HANs and HKTs decreased with increasing pH. Specifically, HAN levels declined from 3.79 μg/L at pH 7.5 to 0.61 μg/L at pH 9.5, consistent with previous findings involving free chlorine.[75] After a 3 h reaction, HKT concentrations decreased from 11.4 μg/L at pH 3.5 to 3.50 μg/L at pH 9.5. The increase in THM formation at higher pH is likely due to more efficient halogenation of ketones and their subsequent cleavage via the haloform reaction, which is promoted under basic conditions due to enhanced enolate formation.[76] Results indicate that 1-chlorobenzotriazole exhibits DBP formation patterns comparable to those observed with free chlorine.

1-chlorobenzotriazole chemistry

According to literature, 1-chlorobenzotriazole (1-Cl BTR) exists in aqueous solutions as an equilibrium mixture of several reactive chlorine species, including protonated 1-chlorobenzotriazole (1-Cl BTRH$^+$), chloronium ion (H_2OCl^+), and chlorine (Cl_2), as shown in Eq. 1-4.[77]

$$1Cl\,BTR + H_3O^+ \rightleftharpoons 1Cl\,BTRH^+ + H_2O \qquad (1)$$

$$1Cl\,BTRH^+ + H_2O \rightleftharpoons BTR + H_2OCl^+ \qquad (2)$$

$$1Cl\,BTRH^+ + Cl^- \rightleftharpoons BTR + Cl_2 \qquad (3)$$

$$H_2OCl^+ + Cl^- \rightleftharpoons H_2O + Cl_2 \qquad (4)$$

$$Cl_2 + 2H_2O \rightleftharpoons HOCl + H_3O^+ + Cl^- \qquad (5)$$

$$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^- \qquad (6)$$

The protonated species, 1-Cl BTRH$^+$ can undergo solvolysis in water to generate H_2OCl^+ due to weakening of the N-Cl bond (Eq. 2). Additionally, both 1-Cl BTRH$^+$ and H_2OCl^+ can react with chloride ion (Cl^-) to release Cl_2 as shown in Eq. 3 and 4.[77] It has been proposed that 1-Cl BTRH$^+$ and Cl^- can form a complex as shown in Figure S16 in the SI.[77] The rate of Cl_2 formation increases with excess Cl^-, consistent with previous reports on the Orton rearrangement of halogenoamides.[78]

Cl_2 can then hydrolyze to HOCl (Eq. 5), with a reported concentration-based equilibrium constant of 2.56×10^{-4} M^2.[79] HOCl can further deprotonate to hypochlorite ion (OCl^-) (Eq.6, pKa = 7.50).[79] The relative abundance of the chlorine species is strongly pH-dependant.[79] At low pH (pH<~0.4), Cl_2 predominates, while at pH values up to 7.50, HOCl is dominant, and above pH of 7.50, OCl^- becomes the major species.[79] Also, H_2OCl^+ is considered a transient kinetic intermediate and is unlikely to accumulate under equilibrium conditions.[79] Mass spectrometry data from this study showed increasing peak intensities corresponding to 1-chlorobenzotriazole with decreasing pH (Figure S7 in the SI), consistent with the proposed mechanism. Additionally, these peaks were only observed under excess HOCl, conditions that would drive the equilibrium towards 1-chlorobenzotriaozle.

The DBP formation potential observed from 1-chlorobenzotriazole treatment can be explained by its unique aqueous chemistry, which enables it to act as a dynamic reservoir of free chlorine species. Unlike NH_2Cl, 1-chlorobenzotriazole undergoes protonation and solvolysis to form reactive intermediates such as H_2OCl^+ and Cl_2, ultimately leading to the *in situ* generation of HOCl and OCl^-. This chemical behavior allows 1-chlorobenzotriazole to mimic the oxidative capacity of free chlorine, consistent with the similar DBP concentrations and speciation patterns observed in 1-chlorobenzotriazole and HOCl treatment across different NOM and wastewater matrices. The observed elevated THM levels in SRHA and SRNOM under 1-chlorobenzotriazole treatment—exceeding those of HOCl—further suggest that 1-chlorobenzotriazole not only mimics but may also sustain free chlorine activity through slow and continuous release of oxidizing species, enhancing halogenation over time. Conversely, the lower THM and HAL concentrations in SWE under 1-chlorobenzotriazole relative to HOCl are likely due to differences in precursor composition and the chlorine demand of the matrix, which influence the extent and rate of halogenation reactions. Furthermore, 1-chlorobenzotriazole showed a lower tendency to form tri- and tetra-substituted HKTs, as discussed in the HKT section, reinforcing this interpretation. Results confirm that 1-chlorobenzotriazole functions as a precursor-dependent oxidant capable of maintaining residual free chlorine, with its DBP formation potential governed by its equilibrium chemistry and interaction with organic matter, consistent with its dual role as both a halogen donor and an organic halamine.

Other organic *N*-halamines are also known to release HOCl through hydrolysis of their *N*–Cl bonds including chlorocyanurates, chlorinated hydantoins, *N*-chlorosuccimide, and trichloromelamine.[80] The equilibrium constants for the first hydrolysis step leading to HOCl release are reported as 2.54×10^{-4} for dichlorodimethylhydantoin and 1.6×10^{-4} for trichloroisocyanuric acid, indicating that both compounds exhibit similar HOCl to *N*-halamine ratio. In comparison, NH_2Cl has a significantly smaller hydrolysis equilibrium constant (5×10^{-12}),[81] reflecting its greater stability as a *N*-halamine species. Additionally, chlorocyanurates have been reported to react similar to $HOCl/OCl^-$ in the pH range of 6-9, whereas chlorinated hydantoins are effective at acidic pH and largely ineffective at pH $\geqq 9$. In contrast, 1-chlorobenzotriazole exhibits HOCl-like reactivity across a broad pH range (pH 3.5-9.5; Figure 5), producing similar DBPs to HOCl, suggesting that the equilibrium constant for hydrolysis of 1-chlorobenzotriazole may be higher than chlorocyanurates and chlorinated hydantoins, although it requires further investigation.

ENVIRONMENTAL SIGNIFICANCE

BTR-based compounds are widely used in industrial, commercial, and domestic applications, leading to their frequent detection in surface waters and wastewater-impacted environments. While the persistence and toxicity of BTR have been previously documented, their transformation during water treatment processes—and the potential for DBP formation—remains an emerging concern. This study provides new insights into the chlorination of BTR, demonstrating that its chlorinated derivative, 1-chlorobenzotriazole, can generate diverse and elevated levels of DBPs. The findings identify 1-chlorobenzotriazole as an overlooked source to halogenated organic contaminants in chlorinated water systems. Although this study employed relatively high concentrations of 1-chlorobenzotriazole to elucidate its reactivity and DBP formation potential, the results provide valuable mechanistic insights into reactions that are likely to occur at environmentally relevant levels. At lower concentrations, 1-chlorobenzotriazole is expected to produce proportionally lower DBP yields. Importantly, the study also shows that 1-chlorobenzotriazole can serve as a stable reservoir of free chlorine in solid form, offering potential advantages in terms of ease of handling, storage, and long-term stability. 1-chlorobenzotriazole could be explored as a chemical disinfectant, particularly in applications such as swimming pools, hot tubs, or remote and rural water systems where conventional chlorine handling is challenging. However, a significant drawback is that 1-chlorobenzotriazole also release BTR in the water, which may pose environmental and health concerns due to its known mild toxicity.

Overall, the findings highlight the dual role of 1-chlorobenzotriazole as both a chlorine-releasing compound and a DBP precursor, emphasizing the need for careful consideration of its use in water treatment applications. Further research into its transformation pathways, DBP profiles, and long-term impacts is essential to fully assess its suitability as an alternative disinfectant.

Conflict of interest

The authors declare NO competing (financial or non-financial) interests, or other conflicts of any kind.

Supporting Information: DBP sample prep procedure and quantification parameters, figures of H NMR for 1-chlorobenzotriazole SWE water quality parameters, and UHPLC MS/MS method details and quantification parameters, UV-Vis spectra of 1-chlorobenzotriazole and NOM/SWE reactions, UHPLC MS/MS chromatograms of reference standards and reaction, peak areas by pH, DBP formation by class, Tables with DBP concentrations by experiment.

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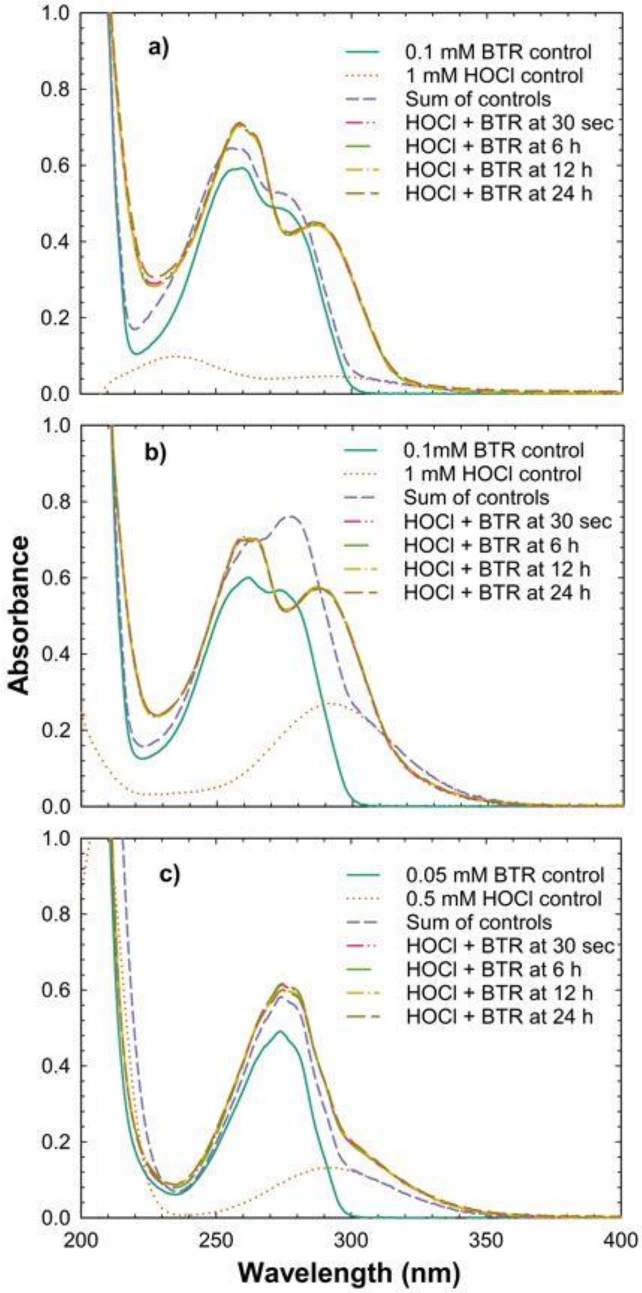

Figure 1. UV-Vis absorption spectra from the reaction between BTR and HOCl (Cl$_2$/ BTR =10:1) from 30 s to 24 h, pH; a) 5.5, b) 7.5, and c) 9.5**,** [Total PO$_4^{3-}$] = 10 mM, [Total CO$_3^{2-}$] = 10 mM, 22 ± 1°C. Sum of controls is the addition of the absorption spectra of BTR and HOCl controls.

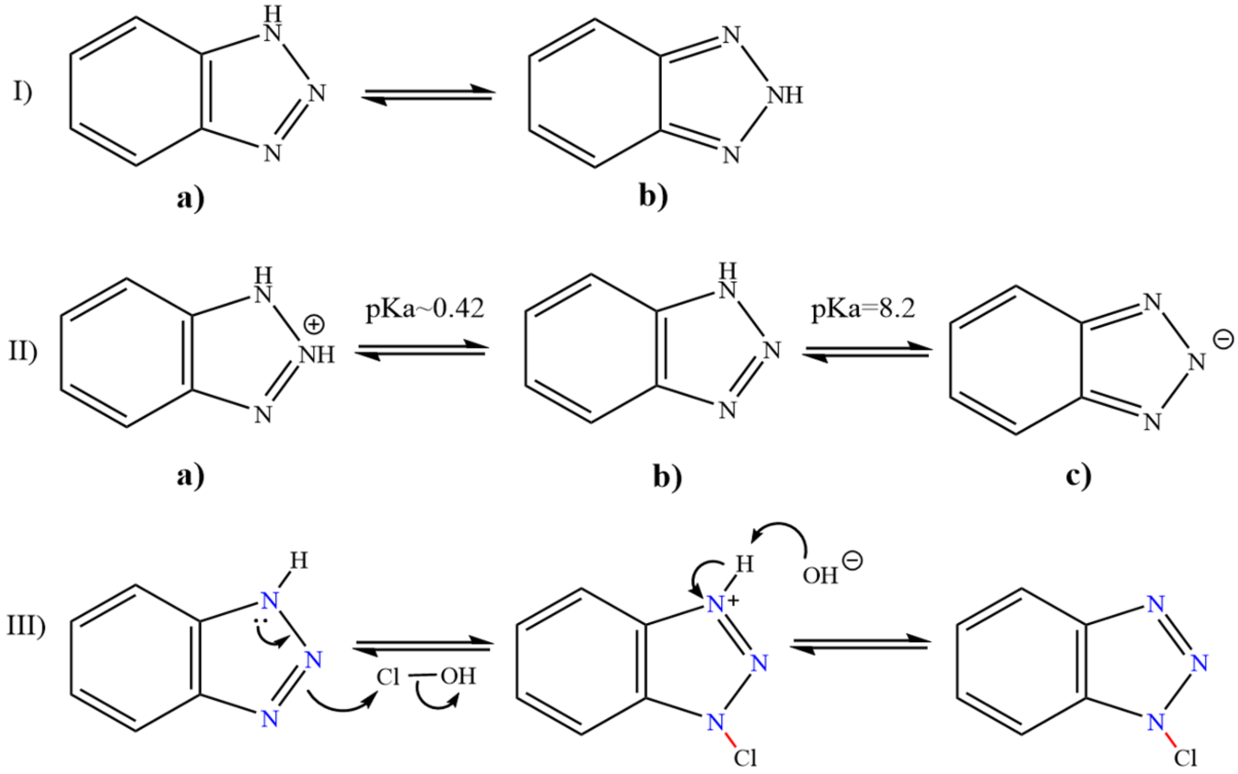

Figure 2. I) Tautomeric forms of BTR a) 1-H BTR b) 2-H BTR. **II)** Resonance structures of BTR; b) benzenoid structure a) and c) quinoid structures. **III)** Proposed mechanism for 1-chlorobenzotriazole formation reaction

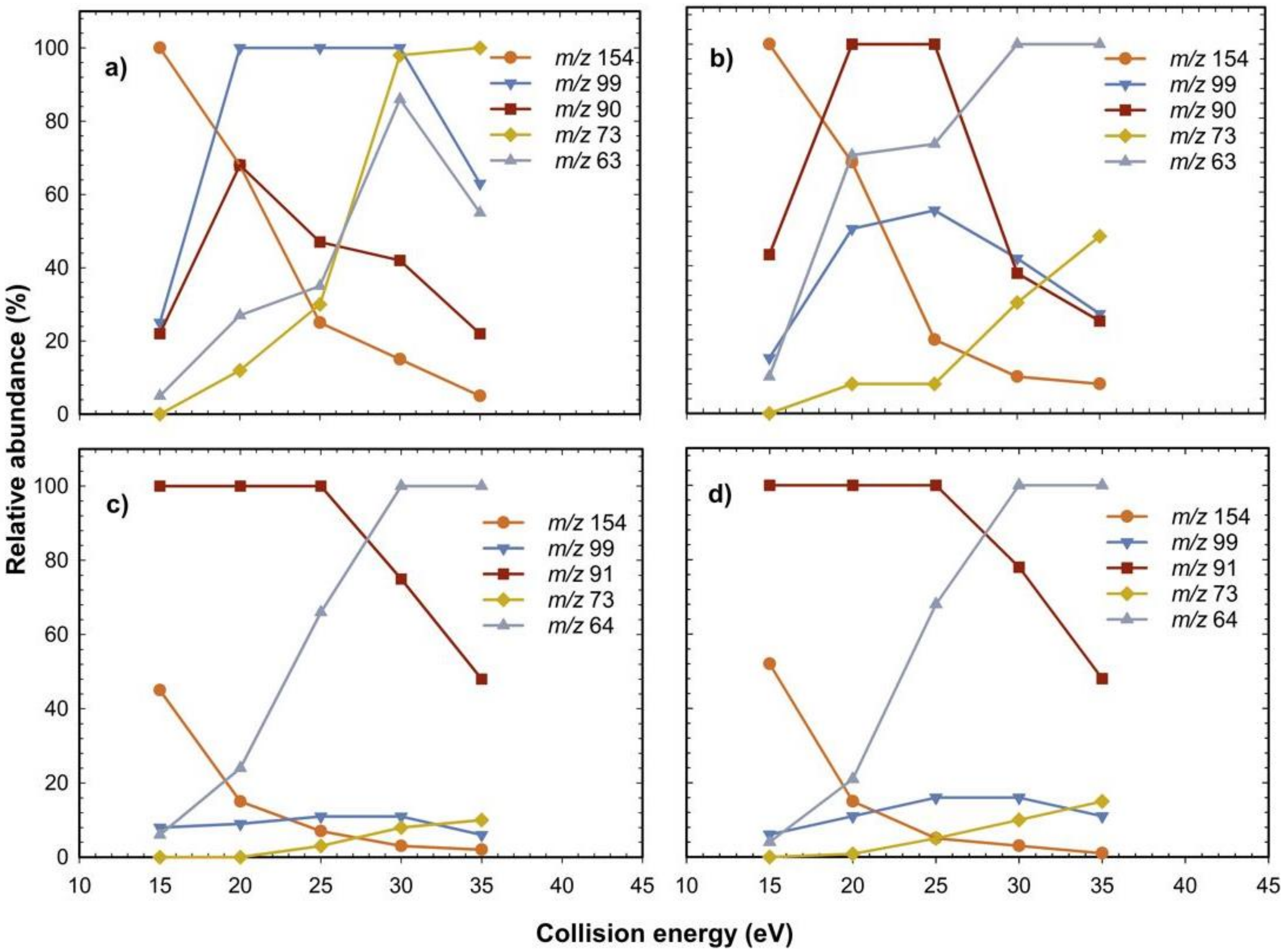

Figure 3. Relative abundance of fragment ions as a function of collision energy. (a) 5-chlorobenzotriazole, (b)7-chlorobenzotriazole, (c) 1-chlorobenzotriazole, and (d) reaction sample with Cl_2/BTR ═ 10:1 at pH 7.5.

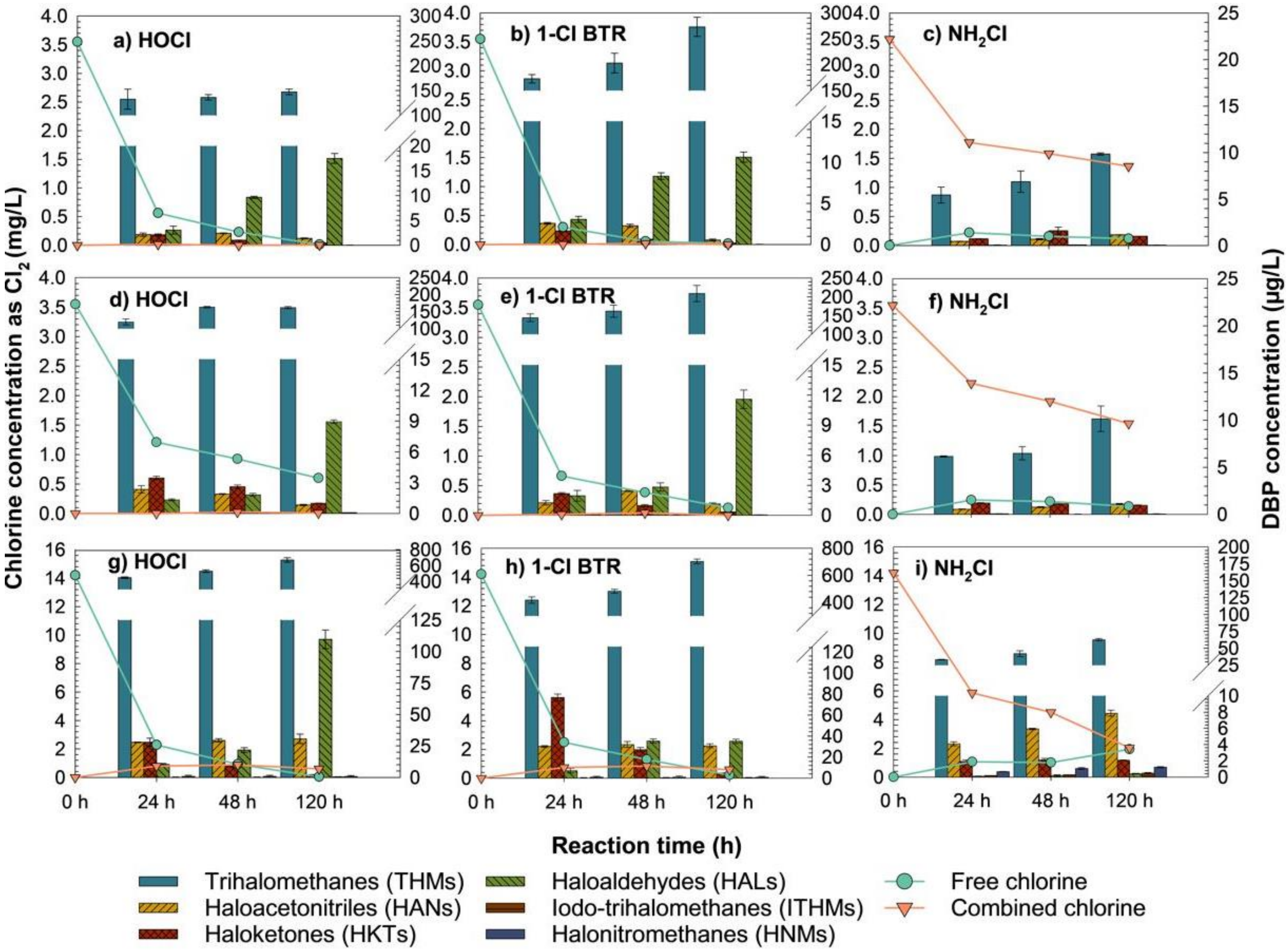

Figure 4. DBP formation in solutions with SRHA (2mg/L as C) reacted with a) HOCl (50 µM or 3.55 mg/L as Cl_2), b) 1-chlorobenzotriazole (1-Cl BTR) (50 µM), c) NH_2Cl (50 µM). DBPs formation in solutions with SRNOM (2mg/L as C) treated with d) HOCl (50 µM), e) 1-Cl BTR (50 µM), f) NH_2Cl (50 µM). DBPs formation in solutions with SWE (TOC = 9.6 mg/L) treated with g) HOCl (200 µM or 14.2 mg/L as Cl_2), h) 1-Cl BTR (200 µM), i) NH_2Cl (200 µM) at pH 7.5, [Total PO_4^{3-}] = 10 mM, 25 ± 1°C. Error bars indicate the standard deviation of replicate measurements (n = 3)

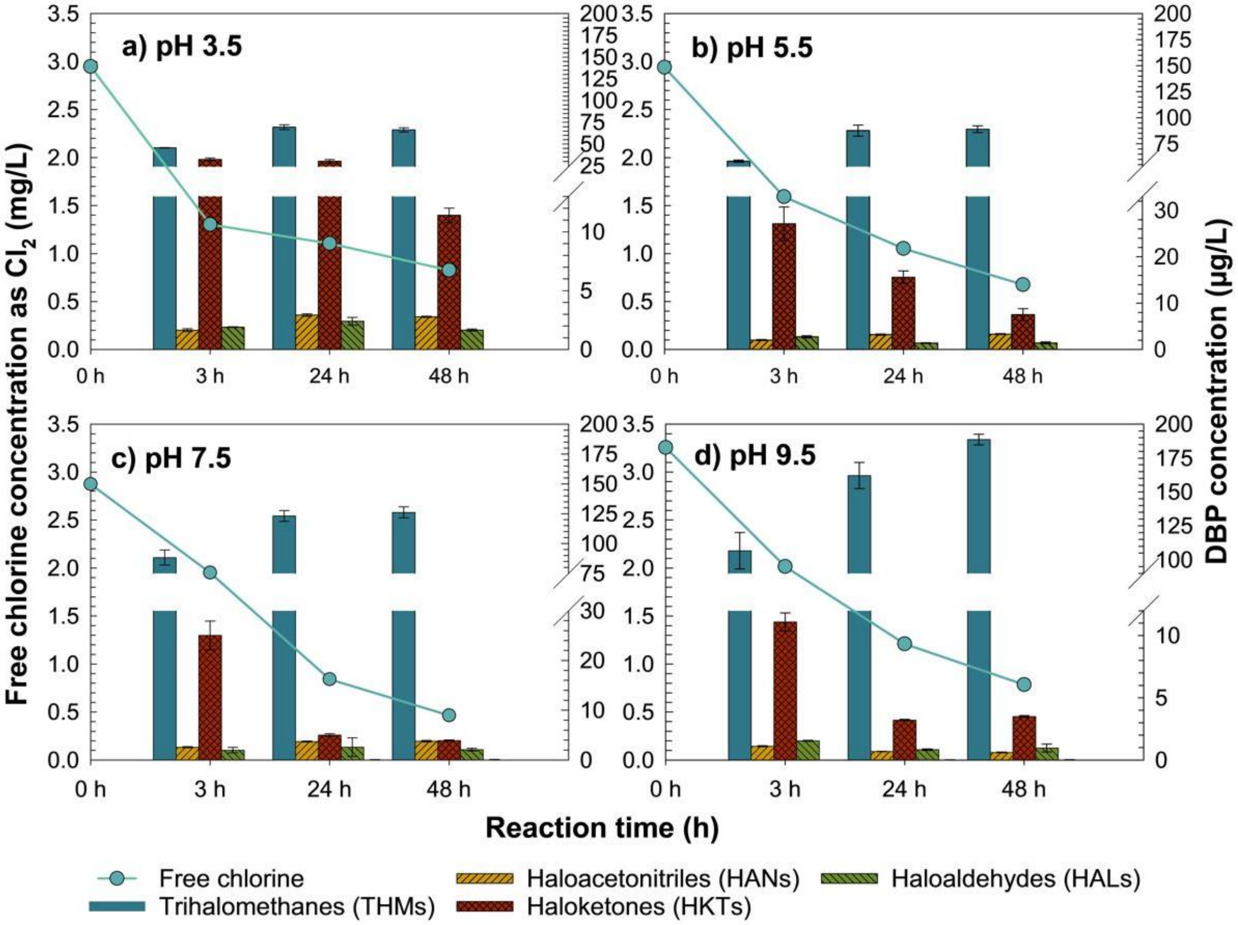

Figure 5. DBPs formation in solutions with SRNOM (2mg/L as C) treated with 1-Cl BTR (50 µM or 3.55 mg/L as Cl_2) at pH a) 3.5, b) 5.5, c) 7.5, d) 9.5, [Total PO_4^{3-}] = 10 mM, [Total CO_3^{2-}] = 10 mM, 25 ± 1°C. Error bars indicate the standard deviation of replicate measurements (n = 3)

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