Journal of Hazardous Materials 199–200 (2012) 73–81

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Oxidation of synthetic phenolic antioxidants during water chlorination

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ARTICLE INFO

Article history:
Received 18 November 2010
Received in revised form 20 October 2011
Accepted 21 October 2011
Available online 29 October 2011

Keywords:
Phenolic antioxidants
Butylated hydroxytoluene (BHT)
Butylated hydroxyanilose (BHA)
Chlorination
By-products
Environmental fate
Gas chromatography–mass spectrometry (GC–MS)

ABSTRACT

The degradation of seven phenolic antioxidants and metabolites during chlorination was investigated. Under strong chlorination conditions (10 mg L^{-1} chlorine, 24 h), five of the target compounds were significantly degraded, while only BHT-Q (2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione) and BHT-CHO (3,5-di-*tert*-butyl-4-hydroxybenzaldehyde) were stable. The effect of the presence of bromide to the sample was only significant for BHA (butylated hydroxyanisole) resulting in increased disappearance rate as it is increased. Moreover, the disappearance kinetics were investigated at different concentrations of chlorine and pH of sample using a factorial experimental design. It was observed that the pH of the sample was a significant factor for BHT (butylated hydroxytoluene) and BHA, and chlorine concentration was significant for BHT, resulting in increased disappearance kinetics as they are increased. The degradation of these compounds has revealed two main processes: hydroxylation and oxidation of the aromatic system. The hydroxylated derivatives in some cases (e.g. from BHT-OH (2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol) and BHT-COOH (3,5-di-*tert*-butyl-4-hydroxybenzoic acid)) are formed via the chlorinated and/or brominated intermediate. Moreover, the oxidation of the aromatic system leads to the quinone derivatives. The investigation of these by-products in real samples by solid-phase extraction–gas chromatography–mass spectrometry (SPE–GC–MS) showed that derivatives of BHT, BHT-OH and/or BHT-COOH occurred in wastewater and drinking water samples analysed.

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1. Introduction

Antioxidants are substances which prolong the shell-life of foodstuffs by protecting them against deterioration caused by oxidation, such as fat rancidity and colour changes. However, the use of antioxidants is not restricted to foodstuffs. They are permitted in many types of packaging materials, in adhesives that come in contact with food and also in cosmetics, personal care products and pharmaceuticals. The most frequent synthetic antioxidants used are the phenolic antioxidants: butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ).

The results of scientific studies about the effects of consumption of these additives to human health are controversial, since several studies have shown a potential link between BHA, BHT and cancer [1,2], while other studies have shown no link [3,4], and even a protective effect [5].

These compounds have been detected in river, ground and wastewater samples. Levels of these compounds were typically in the 10–2000 ng L^{-1} range, depending on the sample nature [6]. In spite of these findings, there is few data on ecotoxicological risks. Moreover, their degradation products should also be evaluated since they may pose an environmental or human health risk [7].

Studies on the metabolism of BHT have revealed that there are two main metabolic processes [8]; that is, oxidation of the alkyl substituent and oxidation of the aromatic ring system. 3,5-Di-*tert*-butyl-4-hydroxybenzoic acid (BHT-COOH) is a major metabolite formed by oxidation of the alkyl substituent and may be generated via the corresponding alcohol (BHT-OH) and aldehyde (BHT-CHO). Moreover, oxidation of the π-system of BHT leads, among others, to 2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (BHT-Q). BHT-OH and BHT-CHO have also been identified as BHT photoproducts, among other 9 compounds [9]. The photodegradation mechanisms of BHT proposed were loss of alkylic groups, loss or addition of hydroxyl groups, isomerisation and oxidation processes [9]. Moreover, the oxidation with permanganate of BHT showed the formation of a diversity of both dimeric and monomeric products depending on the oxidation conditions employed [10].

On the other hand, the metabolism of BHA leads to TBHQ formation. As for BHT, the oxidation of BHA afforded both dimeric and monomeric products [11]. The main monomeric product was 2-*tert*-butyl-6-hydroxy-p-benzoquinone (OH-TBQ) which is produced by oxidation of the intermediate 5-*tert*-butylresorcinol.

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doi:10.1016/j.jhazmat.2011.10.058

The aim of this work was to study the chlorination of phenolic antioxidants and some metabolites, bearing in mind that, according to the European Federation of Chlor-alkali Producers, 98% of the drinking water treatment plants (DWTPs) in Europe use chlorination as one of the main disinfection steps in drinking water production [12] and is sometimes used for tertiary treatment of wastewater. Moreover, residual chlorine in tap water can already react with organic pollutants producing unwanted by-products [13,14]. Thus, the reaction kinetics of phenolic antioxidants were investigated in detail at different chlorine dose and pH by means of a experimental design methodology, and the effect of bromide presence was also considered. Also, several transformation products were tentatively identified by gas chromatography–mass spectrometry (GC–MS) and measured at different environmental samples. To our knowledge, there was not published data on chlorination batch tests of the evaluated analytes.

2. Materials and methods

2.1. Chemicals and stock solutions

The structures of the studied antioxidants are presented in Fig. 1. BHT (2,6-di-*tert*-butyl-4-methyl-phenol), BHA (2-*tert*-butyl-4-methoxy-phenol), BHT-COOH (3,5-di-*tert*-butyl-4-hydroxybenzoic acid), BHT-Q (2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione), BHT-OH (2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol) and TBHQ (2-*tert*-butylbenzene-1,4-diol) were obtained from Sigma–Aldrich (Steinheim, Germany) and BHT-CHO (3,5-di-*tert*-butyl-4-hydroxybenzaldehyde) from TCI Europe (Zwijndrecht, Belgium). Deuterated BHT (2,6-di-(*tert*-butyl-d_1)-4-methyl-d_3-phenol-3,5-d_2; BHT-d_7) and *n*-propyl paraben (*n*-propyl 4-hydroxybenzoate-2,3,5,6-d_4; PrP-d_4), used as surrogate internal standards (ISs) were obtained from CDN Isotopes (Quebec, Canada).

Acetone, methanol and ethyl acetate (all of chromatographic analysis grade) were purchased from Merck (Darmstadt, Germany). Hydrochloric acid was purchased from Panreac (Castellar del Vallès, Spain). Pure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA). Potassium bromide was from Merck and ascorbic acid, potassium dihydrogen phosphate, dipotassium hydrogen phosphate and sodium hypochlorite solution (~10%) from Sigma–Aldrich. Sodium hypochlorite stock solutions at the desired level were prepared daily by dilution in Milli-Q water and their concentration was determined using the N,N-diethyl-p-phenylenediamine procedure with photometric detection [15].

Individual stock solutions were prepared in acetone at the 2 mg mL^{-1} level. Mix standard solutions were prepared at the 20 μg mL^{-1} in acetone and subsequently diluted as necessary. Calibration standards were prepared in ethyl acetate.

2.2. Chlorination experiments

Chlorination of antioxidants was performed on 16 mL amber closed vials that were maintained at room temperature (20 ± 2 °C). Parallel control samples (without chlorine) were also measured.

Preliminary experiments to determine the stability of antioxidants were done (two replicates) with 10 mL of Milli-Q water, adjusted to pH 7.1 with a phosphate buffer and spiked with the tested compounds at the 1 μg mL^{-1} level and 10 mg L^{-1} Cl_2. Seven aliquots of 1 mL each were taken at different reaction times and the reaction stopped with ascorbic acid (0.6 mg mL^{-1}). The analytes were extracted by liquid–liquid extraction in 0.5 mL of ethyl acetate. Moreover, the effect of the presence of a high concentration of bromide (100 μg L^{-1}) on the degradation was evaluated. These experiments were also used for identification of chlorination by-products.

Further experiments to study chlorination kinetics were performed in a similar way, but with lower antioxidants concentrations (50 μg L^{-1}) and different concentrations of chlorine (1–10 mg L^{-1}) and pH of sample (5.7–8.3) being considered. In these experiments, five aliquots were taken at different reaction times and the reaction stopped with ascorbic acid.

2.3. GC–MS determination

GC–MS determination was performed on a Varian 450-GC gas chromatograph equipped with an ion trap mass selective detector

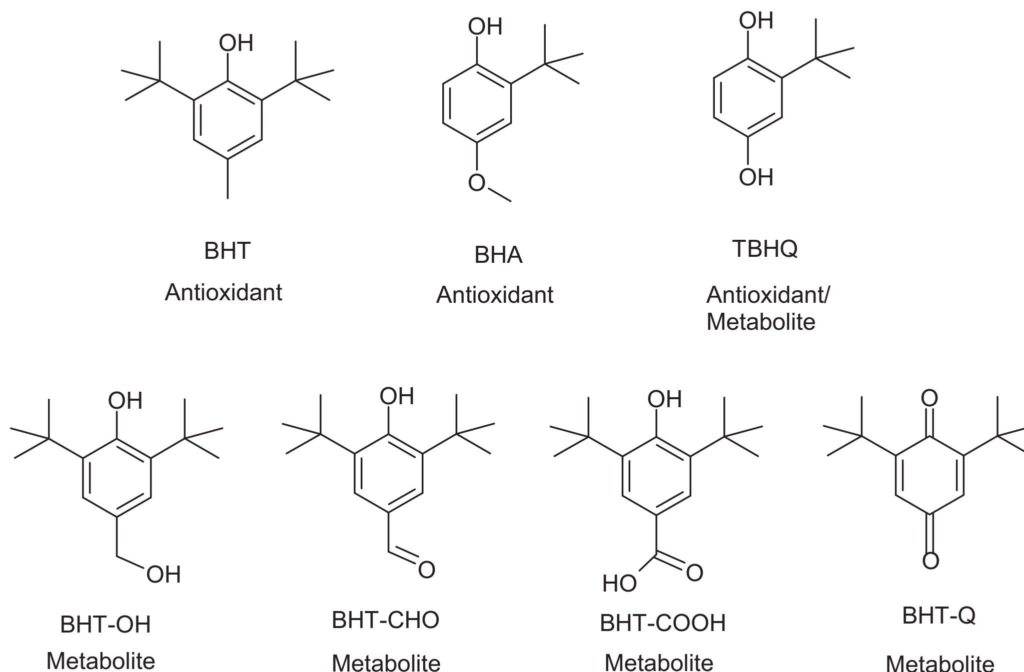

Fig. 1. Structures of the studied antioxidants and metabolites.

Table 1
GC–EI-MS analytical data.

Compound	Retention time (min)	M^+ (m/z)	Quantification ion (m/z)	Qualifier ions (m/z)
BHT-Q	10.80	220	177	220, 205
BHA	10.99	180	165	137, 180
BHT-d_7	11.28	227	212	227
BHT	11.35	220	205	220, 177
TBHQ	11.74	166	151	123, 166
PrP-d_4	12.59	184	125	142
BHT-CHO	14.27	234	219	191, 234
BHT-OH	14.40	236	221	236, 193
BHT-COOH	15.56	250	235	207, 205

Varian-240-MS and a CP-8400 sampler (Varian Chromatography Systems, Walnut Creek, CA, USA). A Varian 1079 programmed temperature vaporization (PTV) injector equipped with a Siltek® deactivated liner with frit (Restek, Bellefonte, PA, USA) was used. The PTV LargeVolume injection mode was used with an initial temperature of 65 °C and a split flow of 75 mL min^{-1} (1 min) and raised at 200 °C min^{-1} in splitless mode to a final temperature of 300 °C and a split flow of 80 mL min^{-1}. The injection volume was 20 μL. An HP-5ms (Agilent Technologies, Palo Alto, CA, USA) capillary column (30 m × 250 μm i.d., 0.25 μm film thickness) was used with the following oven temperature program: 4 min at 70 °C, first ramp at 10 °C min^{-1} to 270 °C and second ramp at 25 °C min^{-1} to 290 °C (held for 10 min). Helium was used as carrier gas with a constant flow of 1 mL min^{-1}.

The ion energy used for electron ionization (EI) in the mass spectrometer was 70 eV. Manifold, ion trap, ion source and transfer line temperatures were maintained at 40, 150, 200 and 290 °C, respectively. Helium was also used as damping gas at a flow of 2.5 mL min^{-1}. The same conditions were also used for positive chemical ionization (PCI), but methane was introduced in the ion source at a pressure of 70 μTorr.

The ion trap MS operated in the mass range 45–500 m/z in the full-scan acquisition mode. The characteristic ions together with the substance-specific GC retention times for each studied compound are shown in Table 1. The NIST 2005 library supplied by Varian was used for the tentative identification of oxidation by-products.

2.4. Software

Experimental design creation and analysis was performed with the software package Statgraphics 5.1 (Statpoint Technologies, Warrenton, VA, USA).

2.5. Samples

All samples were collected in amber glass bottles, previously washed with acetone, methanol and Milli-Q water, in June–July 2010. Subsequently after sampling, they were filtered through 0.45 μm nitrocellulose filters (Millipore) and stored at 4 °C until analysed (within 48 h). Two tap water samples were collected at different points in Santiago de Compostela (Galicia, NW Spain) within a 2 h time period. Ascorbic acid (0.6 mg mL^{-1}) was added to these samples in order to eliminate residual chlorine. Also, two wastewater influent and effluents samples were taken at different days in a wastewater treatment plant located near Santiago de Compostela (Galicia, NW Spain) which receives urban and hospital wastewater from ca. 100,000 inhabitants and processed immediately.

These samples were extracted by solid-phase extraction (SPE) and determined by GC–MS as detailed elsewhere [16], but without derivatisation and by large volume injection. In brief, 200 mL of filtered sample were subjected to SPE on an Oasis HLB 10 mg (cartridge) and eluted with 1 mL of ethyl acetate. This extract was injected and analysed by PTV–GC–MS, as described in Section 2.3.

3. Results and discussion

3.1. Screening of degradable antioxidants

A first chlorination test of the three antioxidants and four metabolites was performed in order to assess their degradability upon chlorination. Thus, they were treated with a 10 mg L^{-1} Cl_2 concentration at neutral pH (7.1). These conditions were considered as a strong chlorination dosage taking also into account that real water samples contain other organic chemicals that may compete with the antioxidants. After 24 h, BHT-Q and BHT-CHO were degraded into an extent lower than 20%, while the remaining chemicals were fully removed.

Thus, the antioxidants selected for further experiments were: BHT, BHA, TBHQ, BHT-OH and BHT-COOH.

3.2. Influence of pH, chlorine and bromide concentration on chlorination kinetics

First, a preliminary kinetic study was performed for all the degradable compounds under the strong conditions described before (10 mg L^{-1} Cl_2 at neutral pH). Seven aliquots were taken at different reaction times. These experiments were repeated with the addition of bromide (100 μg L^{-1}) in order to check any influence of this anion on the reaction kinetics.

The complete disappearance of the analytes was achieved after a reaction time ranging from 15 min for BHT-COOH to 500 min for TBHQ when bromide was not added to the experiments. The effect of the addition of bromide was only significant for BHA, resulting in increased degradation rate. Fig. 2 shows the kinetic profiles with and without bromide for BHA and exemplarily for BHT-COOH.

Then, a study on the pH and chlorine influence on the oxidation of the analytes was carried out by an experimental design methodology [17–19]. This strategy permits evaluating not only the factors influencing the degradation of antioxidants but also the interaction between these factors [20]. Provided that bromine concentration was only an important factor for BHA, the factors considered were

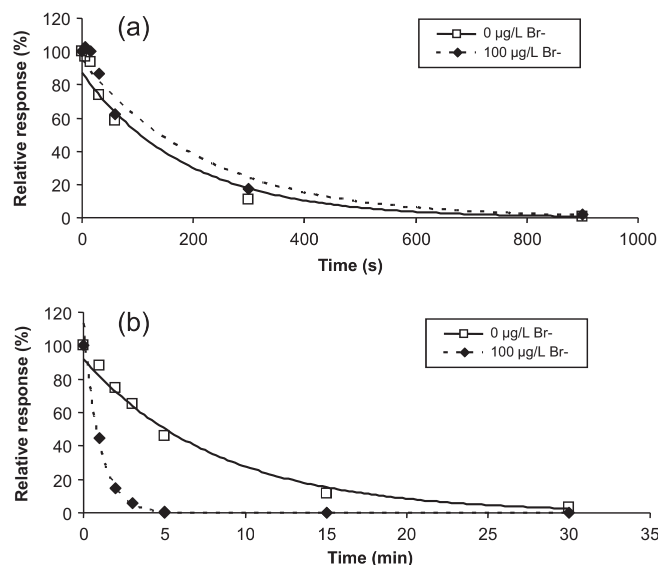

Fig. 2. Time profiles of (a) BHT-COOH and (b) BHA degradation upon chlorination. Experimental conditions: 1 μg mL^{-1} analytes, 10 mg L^{-1} Cl_2, pH 7.1.

Table 2
Factorial 2^2 design experimental plan and measured pseudo-first order kinetics half-lives ($t_{1/2}$).

Exp. No.	pH	Chlorine (mg L^{-1})	$t_{1/2}$ (min)					
			BHA (0 μg L^{-1} Br$^-$)	BHA (100 μg L^{-1} Br$^-$)	BHT	TBHQ	BHT-OH	BHT-COOH
1	7	5.5	6.5	0.68	66	209	9	1.00
2	5.7	1	26	10.2	244	3755	132	30.57
3	5.7	10	23	4.2	54	1266	20	0.47
4	8.3	1	7.5	2.4	37	442	104	2.65
5	8.3	10	1.2	0.15	13	43	3	0.38
6	7	5.5	7.4	0.61	59	215	10	0.87

pH (5.7–8.3) and chlorine dose (1–10 mg L^{-1} as Cl_2) as mentioned in the experimental section. The experimental levels were selected according with the environmental expected values and the typical chlorine concentrations employed during water treatment. This study was done by means of a factorial 2^2 experimental design. The experimental points, selected by using the factorial 2^2 experimental design, are located at the corners and at the centre of the experimental domain, with the shape of a square. The experimental plan is shown in Table 2, where experiments 1 and 6 are replicates of the central point. Thus, the final number of experiments was 6, each experiment being sampled at five different times: between 0–30 min (BHA and BHT-COOH), 0–100 min (BHT-OH), 0–300 min (BHT) and 0–3000 min (TBHQ). In the case of BHA, the experimental design was performed at two different levels of bromide concentration: 0 and 100 μg L^{-1}. Then, empirical disappearance half-lives ($t_{1/2}$) were calculated from the pseudo-first order kinetic plots for each experiment and the design analysed for each antioxidant. The correlation coefficients (R) obtained from the logarithmic kinetic plots were usually higher than 0.9. The calculated $t_{1/2}$ values for each analyte are given in Table 2.

For BHA, the two factorial designs were treated together, as a user defined design, in order to estimate the effect of the three factors simultaneously. The results shown in Table 2 ($t_{1/2}$ values) were statistically analysed with a chemometric software. Fig. 3 shows exemplarily the standardized Pareto charts for BHA and BHT. The Pareto chart is a bar graph in which factors are plotted in decreasing order of impact. The significance level corresponds to the vertical line on the chart. Hence, bars extending beyond the line are statistically significant [21]. After experimental analysis, it was observed that pH and bromide concentration were statistically significant with negative effects for BHA (Fig. 3a), meaning that an increase of the pH or bromide concentration leads to significantly lower $t_{1/2}$ values; i.e. faster reaction kinetics. The role of the pH agrees with previously published chlorination studies for other phenolic compounds [13,22], where the higher reactivity of the phenolate ion as compared to neutral phenol dominates the kinetics in spite of the

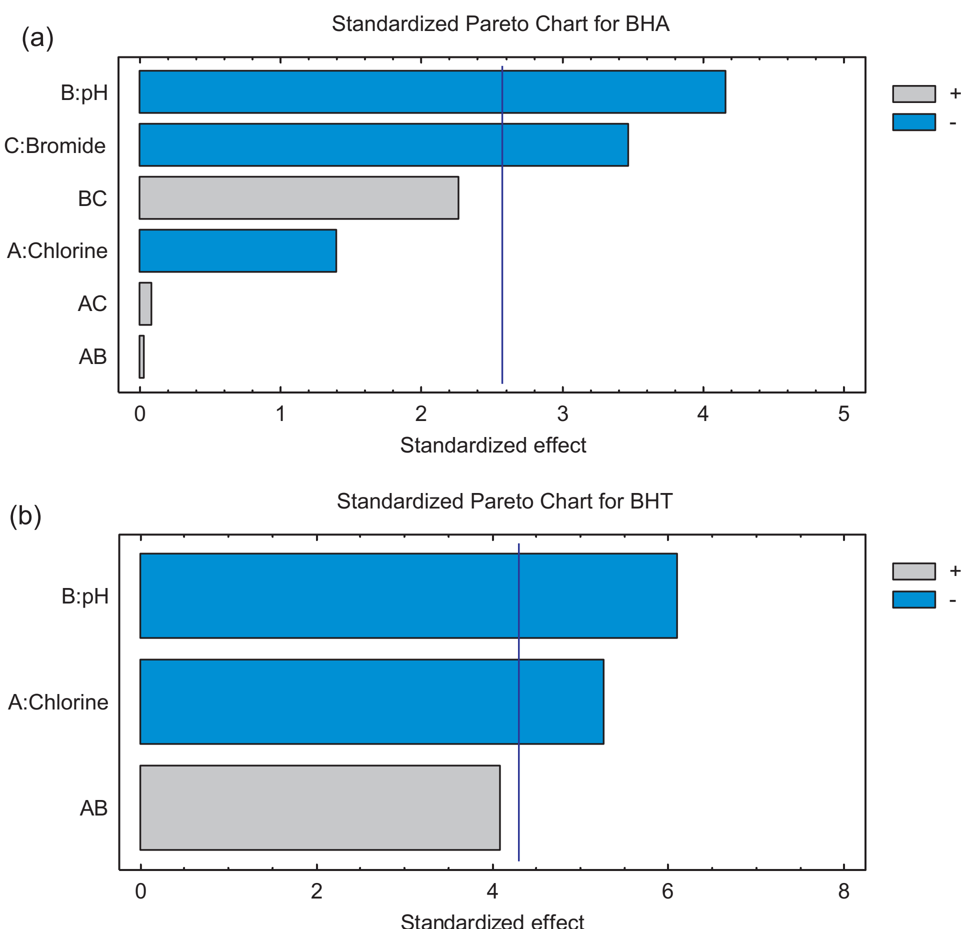

Fig. 3. Pareto charts of (a) BHA and (b) BHT.

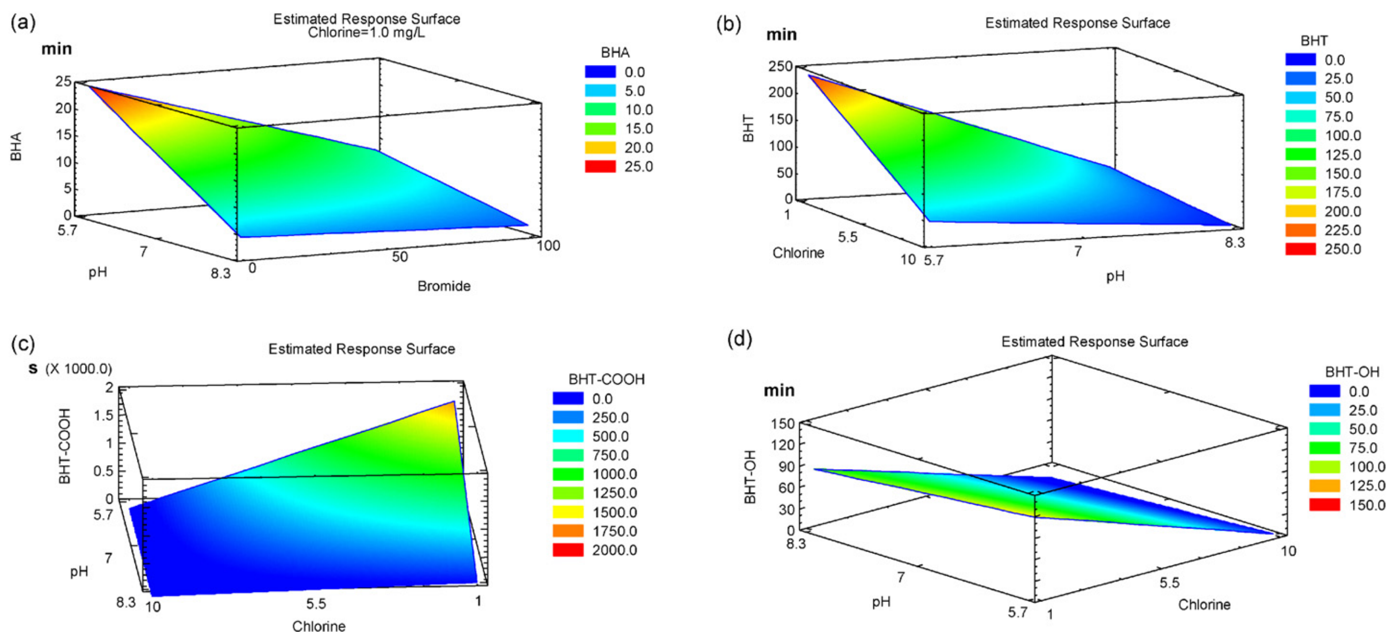

Fig. 4. Response surfaces of (a) BHA, (b) BHT, (c) BHT-COOH and (d) BHT-OH.

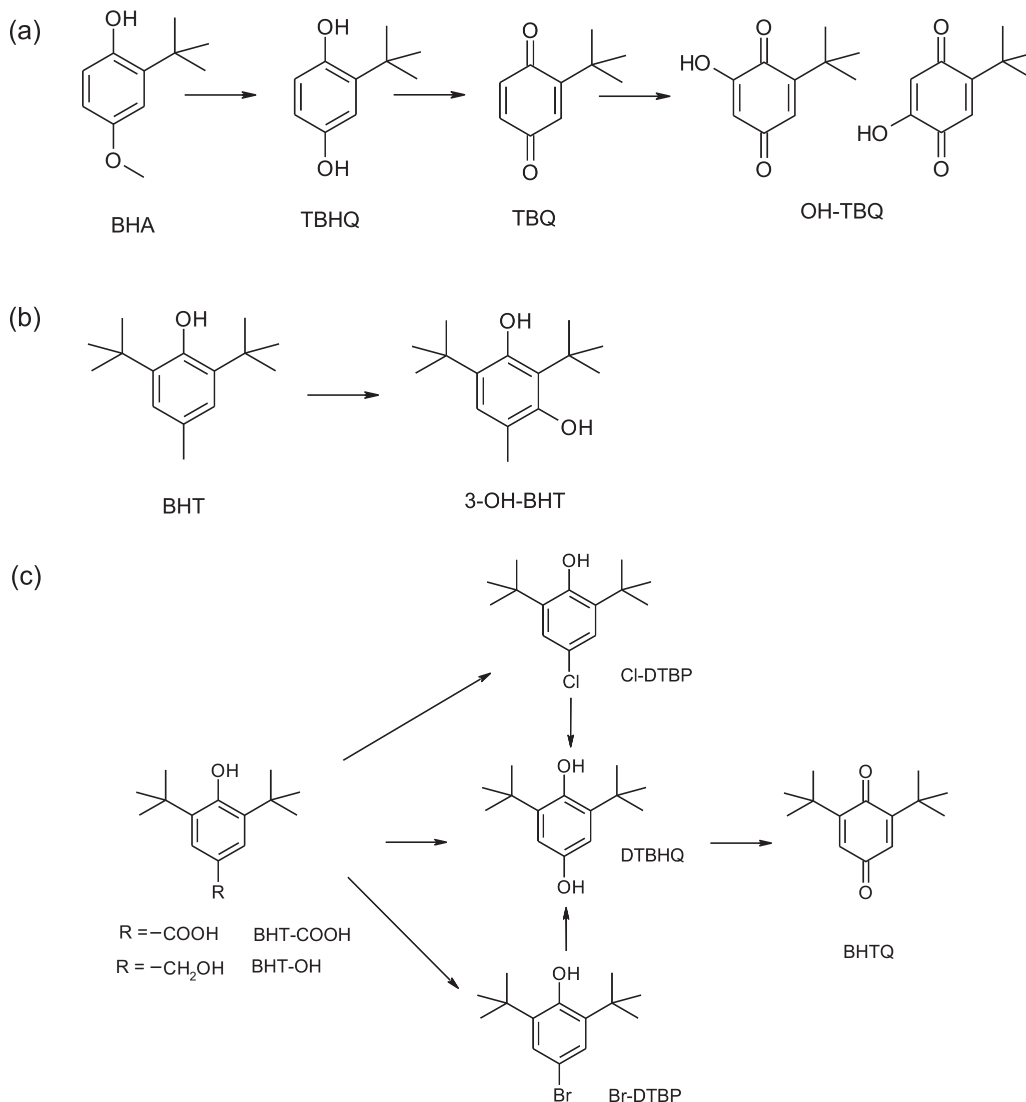

Fig. 5. Proposed degradation patterns of (a) BHA, (b) BHT, and (c) BHT-COOH and BHT-OH.

Table 3
By-products information.

Abbreviation	Name	CAS no	Retention time (min)	M^+ (*m/z*)	Quantification ion (*m/z*)
TBQ	2-*tert*-Butyl-1,4-benzoquinone	3602-55-9	7.2	164	121
OH-TBQ	2-*tert*-Butyl-5 or 6-hydroxy-1,4-benzoquinone	3790-91-8 or 4857-70-9	8.4	180	109, 137
OH-BHT	2,4-*tert*-Butyl-6-methyl-1,3-benzenediol	136634-92-9	10.8	236	165
Cl-DBTP	2,6-*tert*-Butyl-4-chloro-phenol	4096-72-4	12.8	240	225, 227
Br-DBTP	2,6-*tert*-Butyl-4-bromo-phenol	1139-52-2	13.7	284–286	269, 271
DTBHQ	2,4-*tert*-Butyl-benzene-1,4-diol	2444-28-2	13.8	222	207

fact that HClO is a stronger oxidant than ClO^-. The effect of bromide can be interpreted as this compound is degraded much faster with HBrO (from the oxidation of Br^-) than with HClO. A possible reason for this is that an intermediate halogenated product is produced, similarly as BHT-COOH and BHT-OH (see below), which may be the critical step; although such halogenated compounds could not be detected. The other factor considered, chlorine, is far from being statistically significant, but it has also a negative effect. Moreover, the BC term (interaction between pH and bromide concentration) is near the significance level. This fact is shown in the response plot (Fig. 4a) where it can be observed that at low pH the presence of bromide speeds up the reaction kinetic, while at high pH bromide plays a less significant role.

Among the other compounds, it was observed that both chlorine concentration and pH were statistically significant only for BHT (Fig. 3b), with negative values; i.e. the higher the concentration of chlorine or the pH-value, the faster the reaction kinetics, as explained for BHA. The effects of these two factors can be visualised in the response surface plot (Fig. 4b). Particularly it can be observed that the dose of chlorine is more important at low pH. The effect of these factors for the other compounds, although not being statistically significant, was also negative in all cases. The AB term (interaction between chlorine concentration and pH) was close for the significance boundary for TBHQ and BHT-COOH, as shown in Fig. 4c exemplarily for BHT-COOH, so at low pH the dose of chlorine speeds up the reaction kinetic, while at high pH the chlorine dose plays a less significant role. In turn, the AB term is far away from the significance boundary for BHT-OH, so there is no interaction between the factors (Fig. 4d).

3.3. By-products identification

Chlorination by-products of each antioxidant were investigated at the 1 $\mu g\,mL^{-1}$ level, both without and with bromide addition (100 $\mu g\,L^{-1}$) by GC–MS with both EI and PCI. The proposed degradation patterns and information of the by-products detected are shown in Fig. 5 and Table 3, respectively.

Degradation of BHA yielded three intense peaks. The first by-product formed is TBHQ, which is a known biological metabolite of BHA [11] and it is also considered in this study since it is also used as an antioxidant, and could thus be unequivocally identified. Then, degradation of TBHQ affords 2-*tert*-butyl-1,4-benzoquinone (TBQ) by oxidation of the OH- groups, which finally undergoes a hydroxylation reaction (in position 5 or 6) yielding 2-*tert*-butyl-hydroxy-p-benzoquinone (OH-TBQ). TBHQ and TBQ are rapidly formed but they are degraded and at longer reaction times only OH-TBQ is identified in the samples (Fig. 6a). As mentioned, TBHQ was identified in base of the retention time and spectrum since a standard was previously injected and TBQ could be easily identified by searching in the NIST library (Fig. 7c) (reference match of 75.2%). The identification of OH-TBQ was more complex, as there was no positive match on the NIST library (this compound is not included). However, the fragmentation pattern observed was similar to that of TBQ, indicating that the by-product was likely a benzoquinone derivative, but due to the excessive fragmentation in the EI spectra, the molecular ion could not be identified (Fig. 7a). To overcome this limitation, samples were analysed using a softer ionization process, PCI, and the protonated molecular ion $[M+H]^+$ could be identified at *m/z* 181 (molecular mass 180 uma) (Fig. 7b). The PCI spectra showed also the loss of CO and H_2O, indicating the presence of carbonyl and hydroxyl groups in the molecule. Moreover, this compound (OH-TBQ) had already been reported as an oxidation product of BHA in aqueous alkaline solution [11].

Degradation of BHT simply leads to the hydroxylated derivative, 2,4-*tert*-butyl-6-methyl-1,3-benzenediol (OH-BHT), which is stable for long periods of time (Fig. 6b). OH-BHT is not included in the NIST 2005 library and was tentatively identified in base of its spectrum and a molecular ion of 236 (Fig. 7d).

Regarding BHT-OH and BHT-COOH, chlorinated (Cl-DTBP) and brominated (Br-DTBP, when bromide is also added to the medium) intermediates are first formed, which then are transformed to the hydroxylated derivative (DTBHQ). These intermediates are rapidly formed and degraded, finally leading to the quinone BHT-Q by oxidation of the aromatic system, which, as was discussed before (see Section 3.1), is stable under these conditions (Fig. 6c). DTBHQ, Cl-DTBP and Br-DTBP could be easily identified by searching in the NIST library of spectra (reference matches 83.5%, 88.9% and 86.4%

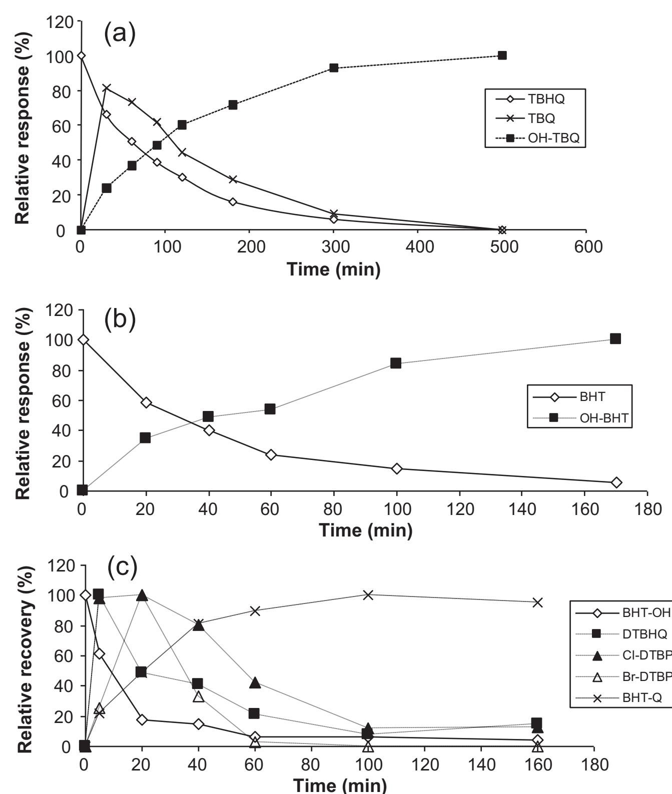

Fig. 6. Time profiles of parent compounds and their by-products (pH 7.1, 10 $mg\,L^{-1}$ Cl_2 and 100 $\mu g\,L^{-1}$ Br^-) for (a) TBHQ, (b) BHT and (c) BHT-OH. Results normalized.

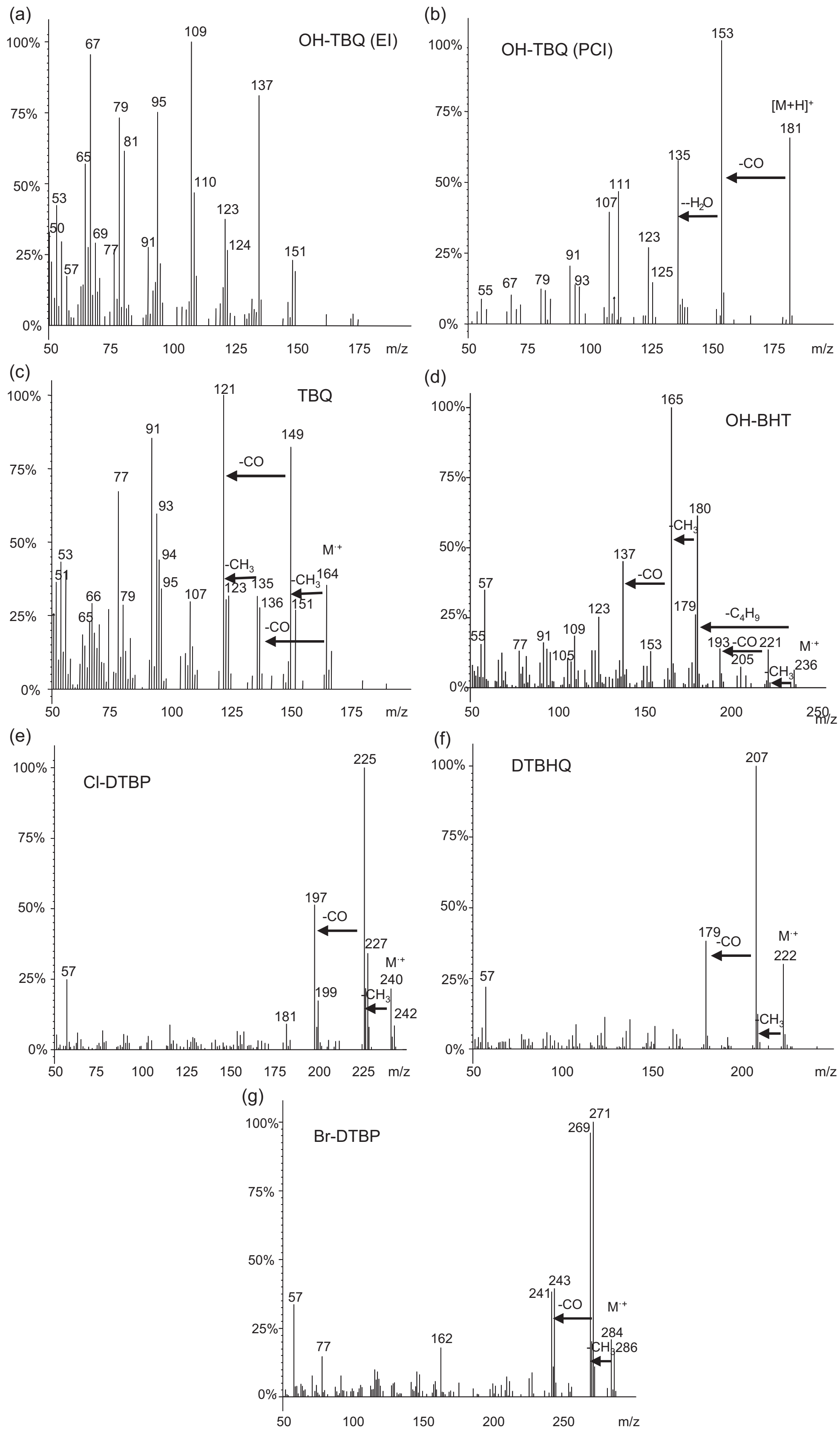

Fig. 7. MS spectra from the chlorination by-products.

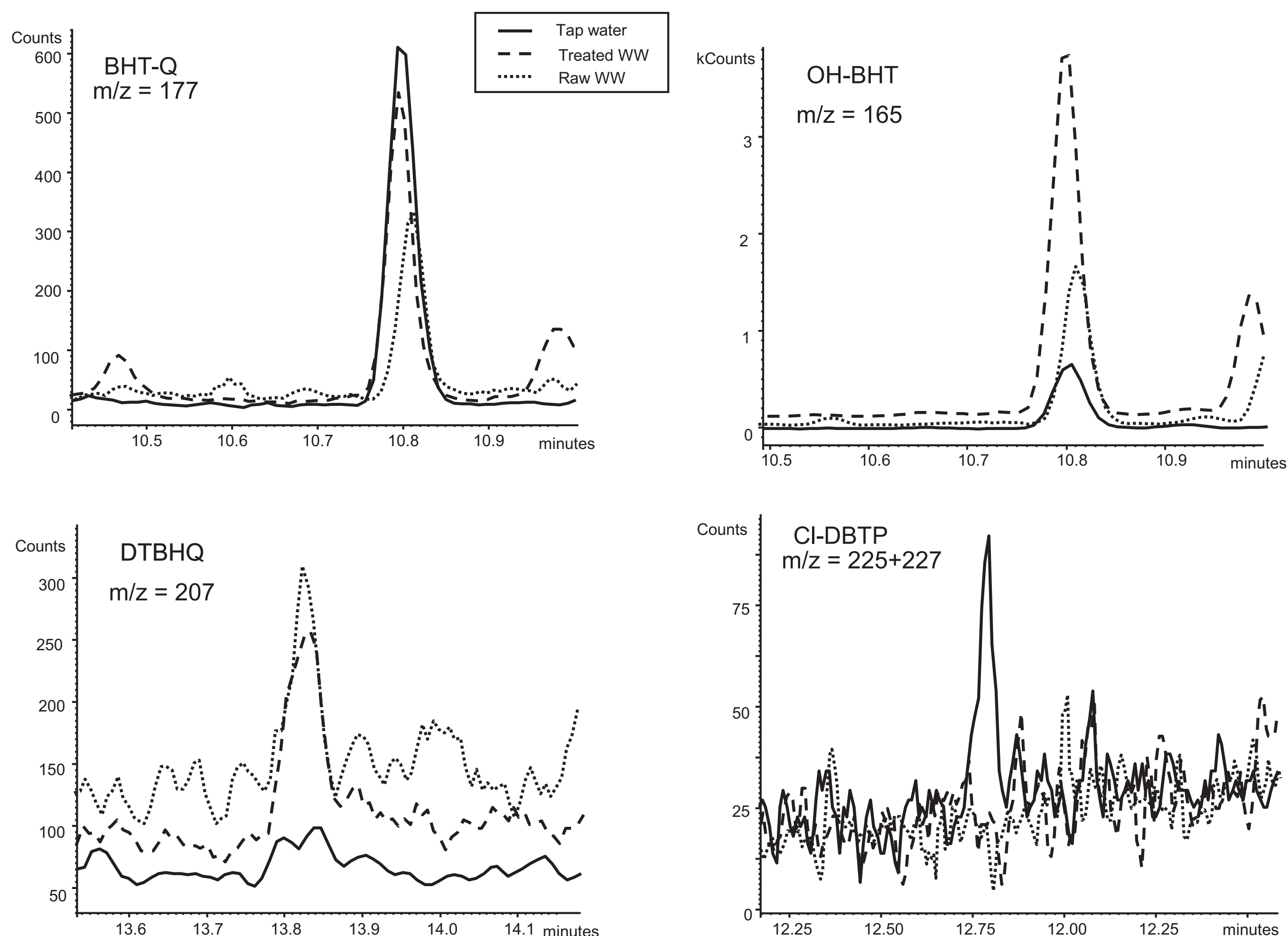

Fig. 8. GC–MS extracted ion chromatograms of the antioxidants by-products in tap water, treated and raw wastewater samples after an SPE 200-fold concentration.

respectively) (Fig. 7e–g). BHT-Q was identified in base of the retention time and spectrum since the pure standard was available.

3.4. Screening of antioxidants and by-products in real samples

Finally, once the by-products were identified, they were screened, together with the parent compounds, for their occurrence in water samples by SPE–GC–MS [16]. Analytes were positively identified by comparing the retention time and the spectrum with those of the chlorination experiments and those for which pure standards were available were quantified. The results of this screening are presented in Table 4.

Two antioxidants, BHT and BHA, were found in wastewater samples at the 37–75 ng L^{-1} level, while only BHT occurred also in tap water at the 12 ng L^{-1} level. On the other hand, TBHQ was not detected in any sample.

Concerning biological metabolites, two of them, BHT-Q and BHT-COOH were identified in all the samples while BHT-CHO and BHT-OH were only detected in raw wastewater samples. Among them, BHT-COOH was the one found at higher concentrations

Table 4
Compounds detected in the samples ($n = 3$). TBHQ, TBQ, OH-TBQ and Br-DBTP were not detected in any of the samples.

Concentration (ng L^{-1}) ± SD						
Compound	Tap water 1	Tap water 2	Treated WW 1	Treated WW 2	Raw WW 1	Raw WW 2
BHT-Q	91 ± 5	10 ± 1	63 ± 4	48 ± 4	35 ± 4	20 ± 2
BHA	–	–	75 ± 1	75 ± 4	56 ± 2	54 ± 1
BHT	12 ± 2	12 ± 1	42 ± 1	71 ± 3	37 ± 4	43 ± 4
BHT-CHO	–	–	–	–	–	20 ± 2
BHT-OH	–	–	10 ± 1	6 ± 1	33 ± 3	78 ± 2
BHT-COOH	13 ± 1	4 ± 1	329 ± 60	339 ± 28	104 ± 12	107 ± 5

By-product/parent area ratio ± SD							
Compound	Parent considered	Tap water 1	Tap water 2	Treated WW 1	Treated WW 2	Raw WW 1	Raw WW 2
OH-BHT	BHT	1.45 ± 0.26	0.90 ± 0.09	3.63 ± 0.39	1.99 ± 0.12	1.67 ± 0.15	1.68 ± 0.06
Cl-DBTP	BHT-COOH	0.32 ± 0.05	–	–	–	–	–
DTBHQ	BHT-COOH	–	–	0.15 ± 0.01	0.11 ± 0.01	0.39 ± 0.05	0.66 ± 0.03
	BHT-OH	–	–	1.41 ± 0.28	1.48 ± 0.15	0.43 ± 0.05	0.25 ± 0.03

in wastewater (100–340 ng L^{-1}) and BHT-Q in tap water (10–90 ng L^{-1}). Indeed, the degradation processes that lead to the formation of BHT-Q are diverse, but oxidation by chlorine should also be taken into account.

Among the chlorination by-products, OH-BHT, Cl-DBTP and DTBHQ were detected in the samples. As an example, the extracted ion chromatograms of tap water, raw and treated wastewater are presented in Fig. 8. Obviously, the concentration of these analytes cannot be calculated, since no standards were available. However, the area ratio of these compounds related to its parent(s) chemical(s) is presented in Table 4. This can give an idea of its expectable concentration. Thus, OH-BHT occurs in the sample at concentrations similar or higher than BHT, and DTBHQ may occur at a level similar to BHT-OH. Cl-DBTP was only found in a tap water sample at a concentration close to its detection limit, which points towards it rapid further degradation to DTBHQ and BHT-Q, as discussed in the previous section.

4. Conclusions and outlook

Among the seven studied phenolic antioxidants only BHT-Q and BHT-CHO were stable, the other five analytes react with hypochlorous acid at significantly high reaction rates. The pH-value as well as the concentration levels of chlorine and bromide influence the degradation routes and kinetics as shown by the experimental design approach adopted. Then by-products have been tentatively identified by GC–MS experiments and by-products of BHT and BHT-OH/BHT-COOH have been detected in analysed wastewater and some tap water samples. Obviously, the relevance of these chemicals in the water environment needs an evaluation of their (eco)toxicity, along with a deeper study of the toxicity of the parent chemicals. Also, other geographical areas need to be investigated for these metabolites and by-products, since BHT and BHA concentrations have already been reported in the literature [6,23].

Acknowledgements

This research was funded by the Spanish Ministry of Science and Innovation (*Ministerio de Ciencia e Innovación*) and *FEDER* funds: project no. *CTQ2009-08377* and *CTQ2010-18927*. RR and JBQ extend their gratitude to the Spanish Ministry of Science and Innovation (*Ramón y Cajal* research program). Finally, we are indebted to Aquagest for kindly providing access to wastewater samples.

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