

## Supporting Information

### Fate of New Persistent Organic Chemical 3,6-Dichlorocarbazole in Chlorinated Drinking Water

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### 43 **Text S1. Chemicals.**

44 The chemical standards of 3,6-dichlorocarbazole (36-CCZ), 1,3,6-trichlorocarbazole (136-CCZ),  
45 and 1,3,6,8-tetrachlorocarbazole (1368-CCZ), both of the purities >98%, were purchased from  
46 Wellington Laboratories (Ontario, Canada). The carbazole derivatives of 9-phenylcarbazole  
47 (PCZ, >98%) and 3,6-bis(tert-butyl)carbazole (36-BtbCZ, >98%), served as internal standards for  
48 instrumental analysis, were purchased from J&K Chemical (Beijing, China). Organic solvents (HPLC  
49 grade) and other chemicals of reagent grade were purchased from Merck and Sigma-Aldrich. Sodium  
50 hypochlorite stock solution (NaOCl, ~852 mg/L (12 mM) as Cl<sub>2</sub>) was prepared by diluting a  
51 concentrated NaOCl solution (4.00-4.99% Cl<sub>2</sub>, reagent grade) and standardized by the DPD ferrous  
52 titrimetric method.<sup>1</sup>

### 53 **Text S2. Transformation products (TPs) identification using the high-resolution MS**

54 *TP identification:* To identify the TPs, 30 mL water sample were first acidified by HCl solution to  
55 pH ~3, and mixed with 10 mL of hexane/ethyl acetate (1:1 v/v). The acidification treatment was to  
56 prevent the dissociation of some hydroxyl or carboxyl groups in the TPs, and to facilitate the  
57 extraction of TPs from water using organic solvents. The mixed solution was ultrasonicated for 10  
58 min at 21 °C. After 15 min, the organic layer was collected, passed through Na<sub>2</sub>SO<sub>4</sub> for removing  
59 residual water and evaporated to dryness. The residue was reconstituted with acetonitrile to a final  
60 volume of 250 µL. The TPs of 36-CCZ were searched on a UPLC–HRMS system composed of a  
61 Dionex Ultimate 3000 liquid chromatograph coupled with a Q Exactive Plus Orbitrap mass  
62 spectrometer (Thermo Fisher Scientific, USA). TPs were separated on a thermo Scientific™  
63 Accucore™ aQ C18 column (2.1×150 mm, 2.6 µm). The mobile phase was 0.1% formic acid in water  
64 (A) and 100% acetonitrile (B). A gradient run was as follows: started at 10% B, increased to 70% B  
65 in 15 min, and then held for 5 min, decreased to 10% B in 0.1 min, and maintained constant for a total  
66 run time of 25 min. The flow rate was 200 µL/min with the constant temperature of 30 °C. The  
67 optimized orbitrap parameters were: negative ESI full scan mode, resolution of 17500, AGC target  
68 of 1×10<sup>6</sup>, maximum injection time of 100 ms, scan range of 75 to 700 m/z, sheath gas flow rate of 40  
69 AU, discharge voltage of 3.2 kV, and capillary temperature of 350 °C. Information-dependent  
70 acquisition of MS/MS spectra were obtained to assist the identification of the TPs. All data were  
71 acquired and processed using Xcalibur 4.1 SP1 software (Thermo Fisher Scientific, USA).

### 72 **Text S3. Quality assurance and quality control (QA&QC)**

73 For the GC–MS analysis, recoveries of the chemicals were assessed by spiking water samples with  
74 a standard solution. Recoveries of 36-CCZ, 136-CCZ, 1368-CCZ as well as the two internal standards  
75 ranged from 94.2% to 102.3% in water samples. Precision was evaluated after replicate analysis of  
76 random samples (n = 5). The relative standard deviations were ranged from 1.3% to 4.9%. The

concentrations of 36-CCZ, 136-CCZ and 1368-CCZ in water samples were calculated according to their corresponding calibration curves with the two internal standards.

During the TPs analysis using the high-resolution MS, product identification should meet four successive requirements. To be specific, these were: (i) the peak signal-to-noise ratio is needed to exceed 10:1, (ii) the measured  $m/z$  value of the molecular ion should be within 5 ppm of the theoretical value; (iii) the Cl isotope pattern of the detected product should match within 5% of the theoretically predicted abundances of its proposed chemical formula; (iv) MS/MS spectrum of the molecular ion of individual product should match well with the proposed chemical structure. Instrument blanks (50  $\mu$ L acetonitrile) were run before and after sample analysis. Control (without chlorine) and blank (with chlorine but without 36-CCZ) treatments run in parallel. No metabolites were found in instrument and the sample blanks.

#### Text S4. Kinetics of 36-CCZ degradation

The degradation kinetics of 36-CCZ in chlorinated water was investigated under the pseudo-first-order rate condition. The initial concentration of 36-CCZ was  $1.2 \pm 0.03 \mu\text{M}$ , and several concentrations of chlorine ranging from 0-120  $\mu\text{M}$  were added. Figure S1 show the plot of  $-\ln([36\text{-CCZ}]_t/[36\text{-CCZ}]_0)$  as a function of reaction time at pH = 7.6. The result show that the kinetic experiments can be well described by a pseudo-first-order kinetics as demonstrated by the linear plots ( $R^2 > 0.98$ ). The reaction order with respect to chlorine was examined at pH 7.6 by varying the chlorine concentrations. The Figure 1b (In the manuscript) shows that the pseudo-first-order rate constant  $k_{obs}$  is linearly correlated to the chlorine dose at pH 7.6. Therefore, the rate of 36-CCZ in chlorine group disappearance was first order to the initial concentration of chlorine and to the 36-CCZ concentration as Eq. (1):

$$-\frac{d[36\text{-CCZ}]}{dt} = k_{app,Cl}[\text{HOCl}]_{tot}[36\text{-CCZ}] \quad (1)$$

where  $k_{app,Cl} = k_{obs}/[\text{HOCl}]_{tot}$  is the apparent second-order rate constants of 36-CCZ in chlorinated water. Subsequently, the 36-CCZ chlorination kinetics can be expressed by Eq.s (2)-(6) as follows:



and the rate expression for the above reaction is

$$-\frac{d[36\text{-CCZ}]}{dt} = k_{Cl-1}[\text{HOCl}][36\text{-CCZ}] + k_{Cl-2}[\text{OCl}^-][36\text{-CCZ}] \quad (5)$$

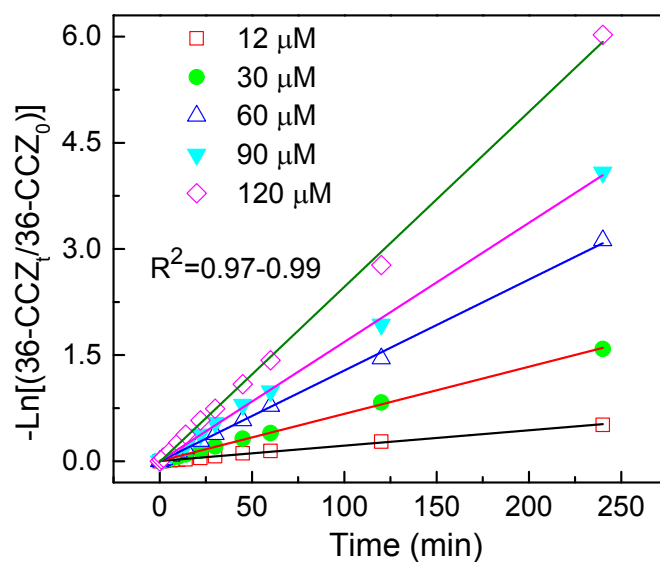
By replacing  $[\text{HOCl}]$  and  $[\text{OCl}^-]$  as ratios of  $[\text{HOCl}]_{tot}$ , the rate of 36-CCZ degradation is

$$-\frac{d[36\text{-CCZ}]}{dt} = k_{\text{Cl-1}}\alpha_{\text{Cl-1}}[\text{HOCl}]_{\text{tot}}[36\text{-CCZ}] + k_{\text{Cl-2}}\alpha_{\text{Cl-2}}[\text{HOCl}]_{\text{tot}}[36\text{-CCZ}] \quad (6)$$

where  $\alpha_{\text{Cl-1}}$  and  $\alpha_{\text{Cl-2}}$  are the fraction of species HOCl and OCl<sup>-</sup> in chlorinated water, respectively.

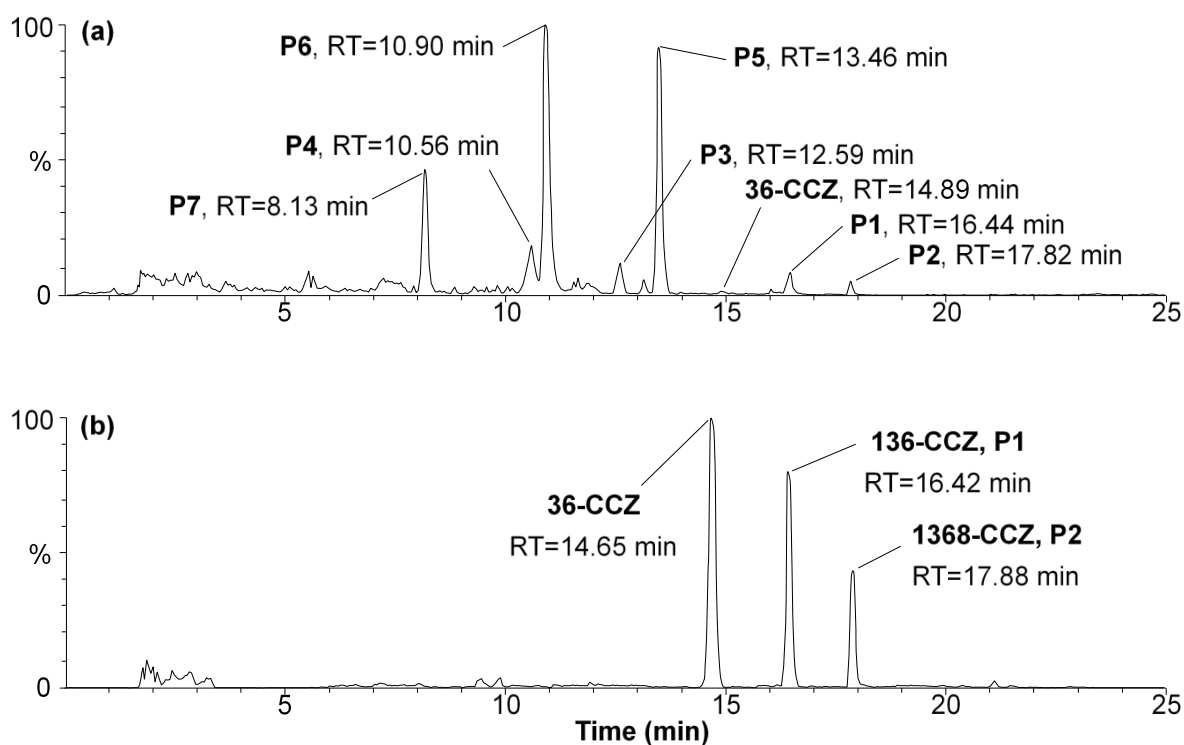
Therefore, by combining [Eq.s \(1\) and \(6\)](#),  $k_{\text{app,Cl}}$  is a function of pH as [Eq.\(7\)](#).

$$k_{\text{app,Cl}} = k_{\text{Cl-1}}\alpha_{\text{Cl-1}} + k_{\text{Cl-2}}\alpha_{\text{Cl-2}} = \frac{k_{\text{Cl-1}}[\text{H}^+] + k_{\text{Cl-2}}k_{\text{a,Cl}}}{k_{\text{a,Cl}} + [\text{H}^+]} \quad (7)$$



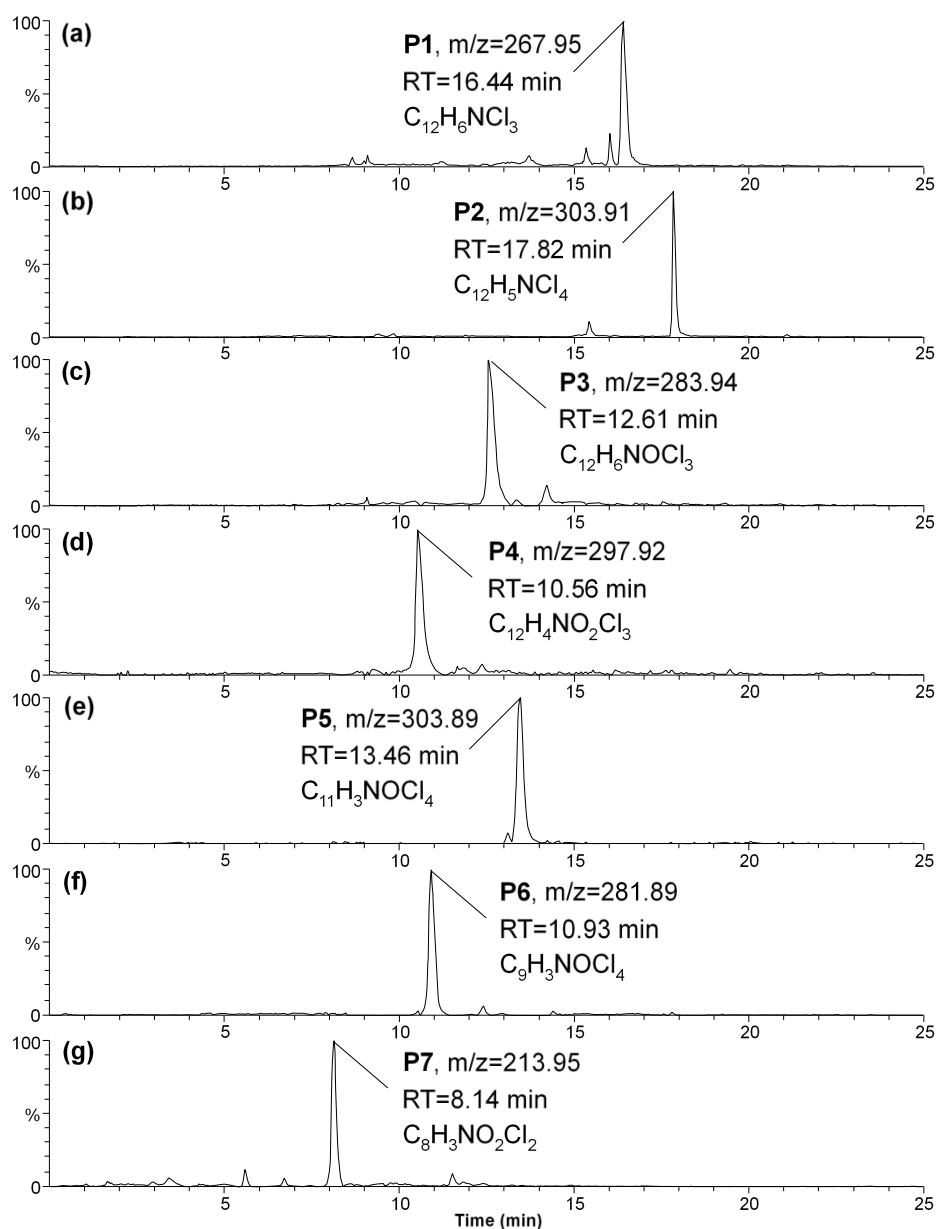
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115 **Figure S1.** Pseudo-first-order kinetic plot of 36-CCZ in chlorinated water at  $20 \pm 1$  °C. Symbols  
 116 represent measured data, and the straight line is the linear regression. Experimental conditions: [36-  
 117 CCZ] $_0 = 1.2 \pm 0.03$   $\mu\text{M}$ , pH = 7.6, and [chlorine] $_0 = 12, 30, 60, 90$  and  $120$   $\mu\text{M}$ .



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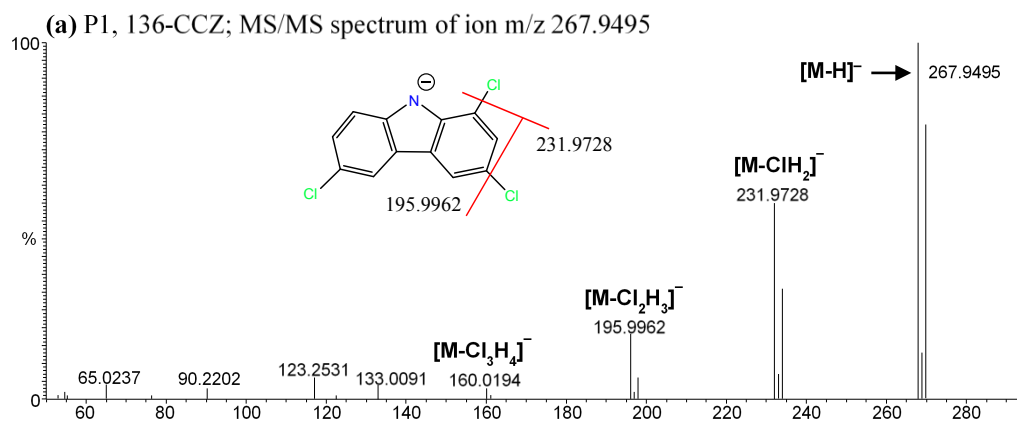
119 **Figure S2.** Products formed after treatment of  $1.2 \pm 0.02 \mu\text{M}$  36-CCZ with  $60 \mu\text{M}$  chlorine at pH 7.6  
 120 (10 mM phosphate) in deionized water for 4 h. (a) Full-scan UPLC–HRMS chromatogram showing  
 121 seven major products P1–P7 at retention times of 16.44 min, 17.82 min, 12.59 min, 10.56 min, 13.46  
 122 min, 10.90 min and 8.13 min. A low peak of the precursor 36-CCZ was found at RT = 14.89 min. (b)  
 123 Full-scan UPLC–HRMS chromatogram of the commercial standards of the 36-CCZ, 1,3,6-  
 124 trichlorocarbazole (136-CCZ) and 1,3,6,8-tetrachlorocarbazole (1368-CCZ).



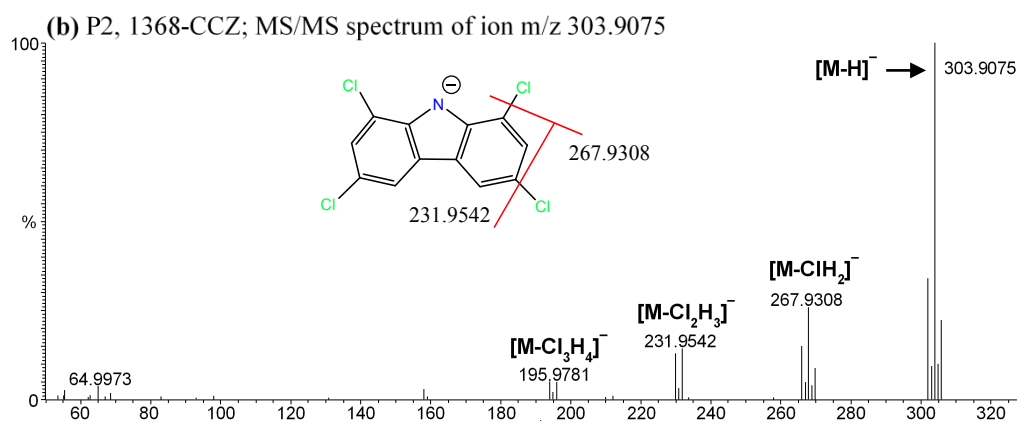
**Figure S3.** Extracted ion chromatograms of the seven detected products of 36-CCZ in chlorinated water samples.



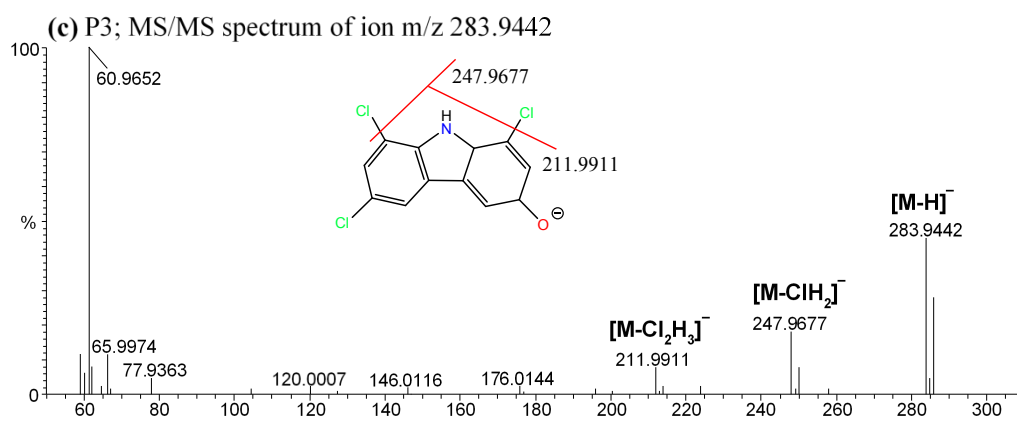
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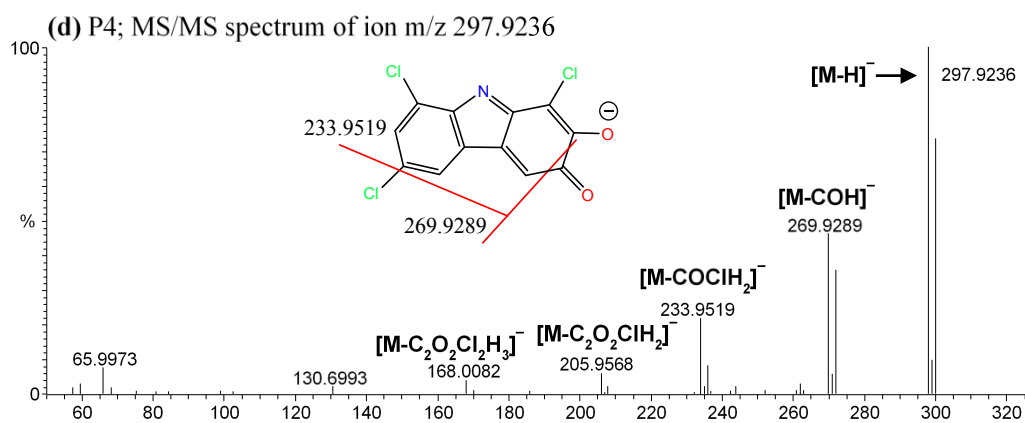
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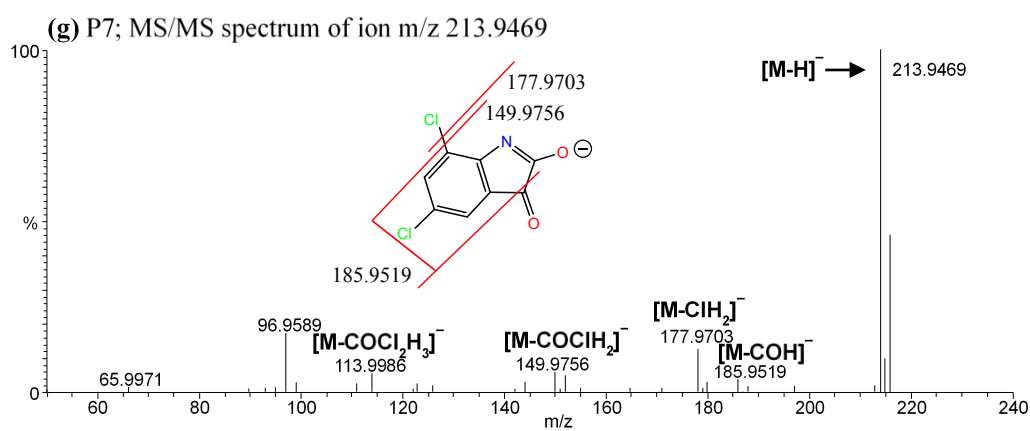
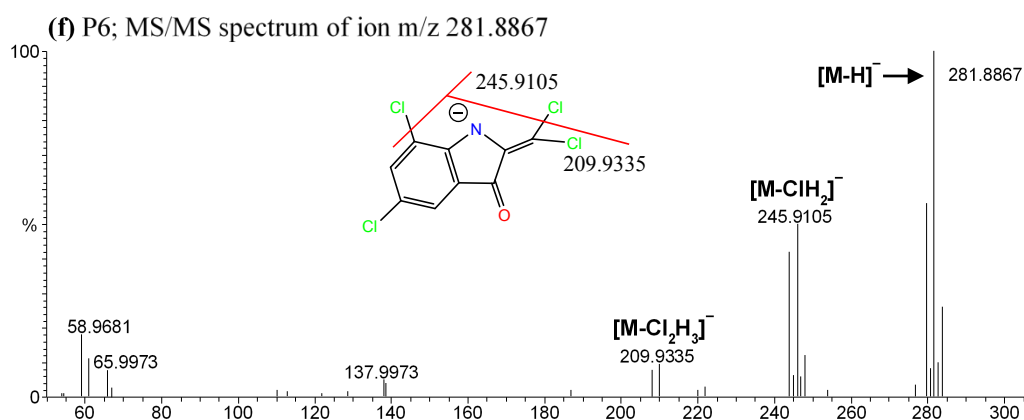
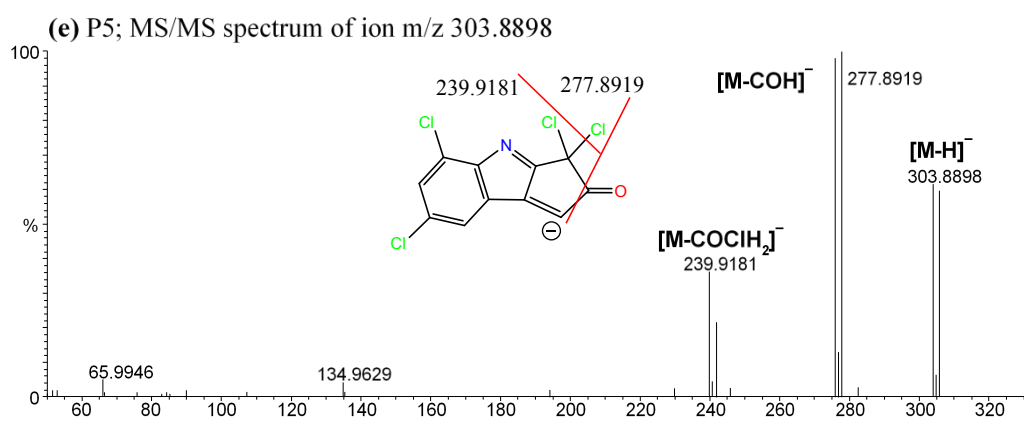


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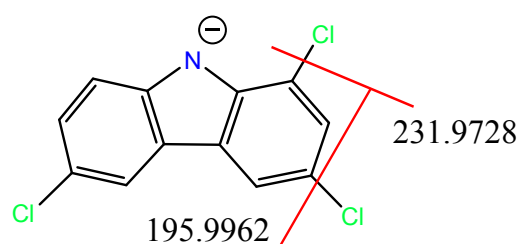


**Figure S4.** MS/MS spectra of the molecular ions for the seven transformation products of 36-CCZ in chlorinated water.

138 **Text S5. Products identification of 36-CCZ in chlorinated water**

139 The UPLC-HRMS system was used to characterize the structures of the seven major products of  
140 36-CCZ in chlorinated water. Separation was achieved using a thermo Scientific™ Accucore™ aQ  
141 C18 column (2.1×150 mm, 2.6 μm) held at 30 °C.

142 **Product P1:** As the description in the manuscript, the product P1 was suggested to be 1,3,6-  
143 trichlorocarbazole (136-CCZ) formed by the chlorine electrophilic attack on the C1 or C8 of 36-CCZ  
144 due to the activated by the “–NH” on the middle heterocyclic ring.<sup>2,3</sup> Figure S5 provides structure of  
145 ionized 136-CCZ, proposed as products consistent with these parent and fragment masses obtained  
146 from the MS/MS spectra by the high-resolution MS analysis.



P1: 1,3,6-trichlorocarbazole

Chemical formula:  $C_{12}H_5NCl_3^-$

Exact Mass:  $m/z = 267.9493/269.9464/271.9434$

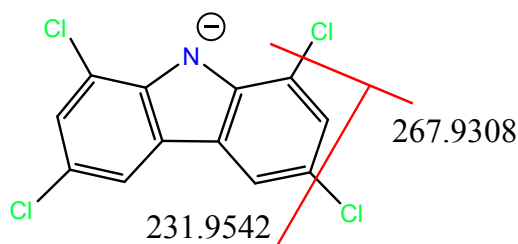
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148 **Figure S5.** Structures of parent and fragment ions for the product P1. Red lines provide the potential  
149 fragmentation cleavage points to produce fragment ions.

150

151 **Product P2:** The extract ion (301.91 or 303.91) chromatogram show the retention time (RT) of P2 at  
152 17.82 min (Figure S3b). The full-scan mass spectrum of the product P2 at retention time of 17.82 min  
153 exhibit molecular ion ( $[M-H]^-$ ) at  $m/z$  301.9105/303.9075/305.9046/307.9018 in the ~8:10:6:1  
154 isotope ratio characteristic of this compound containing four chlorine (Figure 2b). High-resolution  
155 MS analysis resolved the product ion at  $m/z$  301.9105, consistent with an elemental formula of  
156  $C_{12}H_4NCl_4^-$  (exact mass  $m/z$  301.9103; mass shift 1.34 ppm). MS/MS analysis of  $m/z$  303.9075  
157 shows the fragments at  $m/z$  267.9308 and 231.9542, consistent with elemental formulas of  
158  $C_{12}H_3NCl_3^-$  (exact mass 267.9307; mass shift 0.19 ppm) and  $C_{12}H_2NCl_2^-$  (exact mass 231.9540; mass  
159 shift 0.73 ppm), indicating the loss of one and two HCl from the precursor ion (Figure S4b and S6).  
160 According to the results from high-resolution MS analysis, the product P2 was suggested to be  
161 1,3,6,8-tetrachlorocarbazole (1368-CCZ) formed by the chlorine electrophilic attack on the C1 and

162 C8 of 36-CCZ due to the activated by the “–NH” on the middle heterocyclic ring, which was further  
163 verified by the commercial standard (Figure S2b). Figure S7 provides structure of ionized 1368-CCZ,  
164 proposed as products consistent with these parent and fragment masses.



P2: 1,3,6,8-tetrachlorocarbazole

Chemical formula:  $C_{12}H_4NCl_4^-$

Exact Mass:  $m/z = 301.9103/303.9074/305.9044/307.9015$

165

166 **Figure S6.** Structures of parent and fragment ions for the product P2. Red lines provide the potential  
167 fragmentation cleavage points to produce fragment ions.

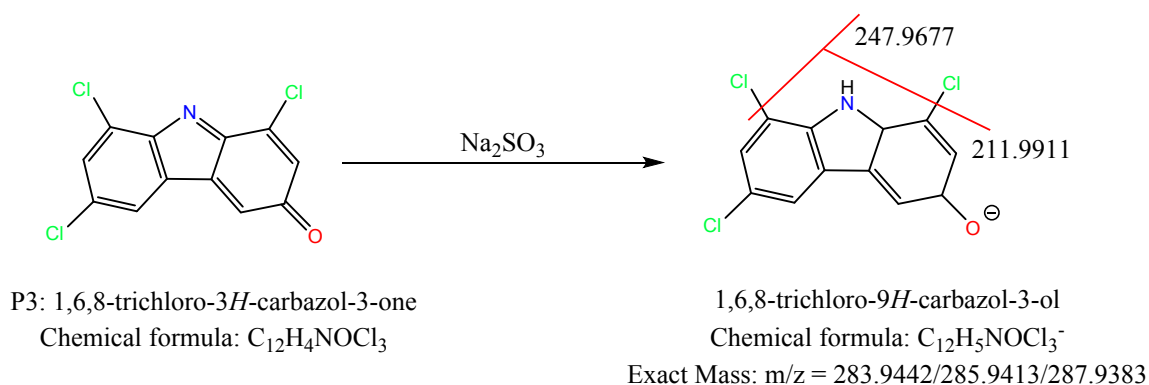
168

169 **Product P3:** The extract ion (23.94) chromatogram show the retention time (RT) of P3 at 12.61 min  
170 (Figure S3c). The full-scan mass spectrum of the product P3 at RT 12.59 min exhibit molecular ion  
171 ( $[M-H]^-$ ) at  $m/z$  283.9442/285.9413/287.9383 in the ~3:3:1 isotope ratio characteristic of this  
172 compound containing three chlorine (Figure 2c). High-resolution MS analysis resolved the product  
173 ion at  $m/z$  283.9442, consistent with an elemental formula of  $C_{12}H_5NOCl_3^-$  (exact mass  $m/z$  283.9441;  
174 mass shift 0.28 ppm). MS/MS analysis of  $m/z$  283.9442 shows the fragments at  $m/z$  247.9677 and  
175 211.9911, consistent with elemental formulas of  $C_{12}H_4NOCl_2^-$  (exact mass 247.9675; mass shift 0.48  
176 ppm) and  $C_{12}H_3NOCl^-$  (exact mass 211.9909; mass shift 0.94 ppm), indicating the loss of one and  
177 two chlorine from the precursor ion (Figure S4c and S7).

178 From the elemental formula of  $C_{12}H_5NOCl_3^-$  and the fragment ions, it is speculated that the  
179 product P3 may be an alcohol structure of 1,6,8-trichloro-carbazol-3-ol (Figure S7), but under the  
180 oxidizing conditions of chlorination, the product P3 is more likely to be a halobenzoquinone-like  
181 structure of 1,6,8-trichloro-carbazol-3-one (Figure S7). The possible reason is that the product P3  
182 (1,6,8-trichloro-carbazol-3-one) was reduced to the corresponding alcohol 1,6,8-trichloro-carbazol-  
183 3-ol by the reaction quenching reagent of  $Na_2SO_3$  for the sample collection before MS analysis  
184 (Figure S7).

185 Considering the mentioned reasons, we speculate that the product P3 of 36-CCZ in chlorinated  
186 water would be 1,6,8-trichloro-3H-carbazol-3-one. It could be formed from the product P2 after the

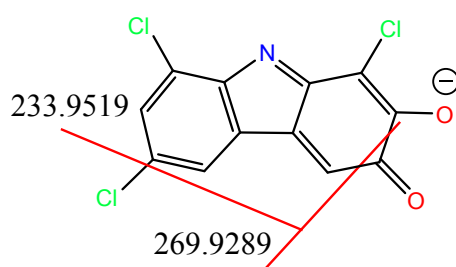
187 reaction of chlorine electrophilic attacks, chlorine elimination, water addition and HCl elimination  
188 (section “**Proposed reaction pathway**” in the manuscript).



189  
190 **Figure S7.** The possible reason for the product P3 (1,6,8-trichloro-3*H*-carbazol-3-one) detected as  
191 the corresponding alcohol (1,6,8-trichloro-9*H*-carbazol-3-ol). Structures of parent and fragment ions  
192 for the corresponding alcohol of product P3 was provided. Red lines indicate the potential  
193 fragmentation cleavage points to produce fragment ions.

194

195 **Product P4:** The extract ion (297.92) chromatogram show the retention time (RT) of P4 at 10.56 min  
196 (Figure S3d). The full-scan mass spectrum of the product P4 at RT 10.56 min exhibit molecular ion  
197 ([M-H]<sup>-</sup>) at m/z 297.9236/299.9206/301.9176 in the ~3:3:1 isotope ratio characteristic of this  
198 compound containing three chlorine (Figure 2d). High-resolution MS analysis resolved the product  
199 ion at m/z 297.9236, consistent with an elemental formula of C<sub>12</sub>H<sub>3</sub>NO<sub>2</sub>Cl<sub>3</sub><sup>-</sup> (exact mass m/z  
200 297.9235; mass shift 0.27 ppm). MS/MS analysis of m/z 297.9236 shows the fragments at m/z  
201 269.9289 and 233.9519, consistent with elemental formulas of C<sub>11</sub>H<sub>3</sub>NOCl<sub>3</sub><sup>-</sup> (exact mass 269.9286;  
202 mass shift 1.29 ppm) and C<sub>11</sub>H<sub>2</sub>NOCl<sub>2</sub><sup>-</sup> (exact mass 233.9519; mass shift 0 ppm), indicating the loss  
203 of the “-CO” and a HCl from the precursor ion (Figure S4d and S8). According to the results from  
204 high-resolution MS analysis, the product P4 was suggested to be 1,6,8-trichloro-2-hydroxy-3*H*-  
205 carbazol-3-one, which would be formed from the product P3 after the reaction of chlorine  
206 electrophilic addition, water addition and HCl elimination (section “**Proposed reaction pathway**” in  
207 the manuscript).



P4: 1,6,8-trichloro-2-hydroxy-3*H*-carbazol-3-one

Chemical formula:  $C_{12}H_3NO_2Cl_3^-$

Exact Mass:  $m/z = 297.9235/299.9205/301.9176$

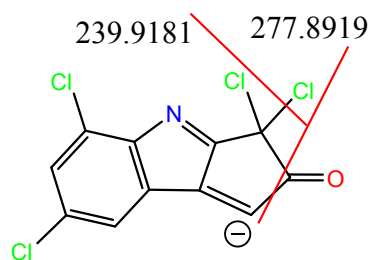
208

209 **Figure S8.** Structures of parent and fragment ions for the product P4. Red lines provide the potential  
210 fragmentation cleavage points to produce fragment ions.

211

212 **Product P5:** The extract ion (303.89) chromatogram show the retention time (RT) of P5 at 13.46 min  
213 (Figure S3e). The full-scan mass spectrum of the product P5 at RT 13.46 min exhibit molecular ion  
214 ( $[M-H]^-$ ) at  $m/z$  303.8898/305.8867/307.8839/309.8811 in the ~8:10:6:1 isotope ratio characteristic  
215 of this compound containing four chlorine (Figure 2e). High-resolution MS analysis resolved the  
216 product ion at  $m/z$  303.8898 consistent with an elemental formula of  $C_{11}H_2NOCl_4^-$  (exact mass  $m/z$   
217 303.8896; mass shift 1.12 ppm). MS/MS analysis of  $m/z$  303.8898 shows the fragments at  $m/z$   
218 277.8919 and 239.9181, consistent with elemental formulas of  $C_{10}H_2NCl_4^-$  (exact mass 277.8917;  
219 mass shift 0.61 ppm) and  $C_{10}HNCl_3^-$  (exact mass 239.9180; mass shift 0.42 ppm), indicating the loss  
220 of the “-CO” and a HCl from the precursor ion (Figure S4e and S9. According to the results from  
221 high-resolution MS analysis, the product P5 was suggested to be 3,3,5,7-  
222 tetrachlorocyclopenta[b]indol-2(3H)-one, which would be formed from the product P4 after the  
223 reaction of electrophilic addition of chlorine, water addition and decarboxylation (section “**Proposed**  
224 **reaction pathway**” in the manuscript).

225



P5: 3,3,5,7-tetrachlorocyclopenta[*b*]indol-2(3*H*)-one

Chemical formula:  $C_{11}H_2NOCl_4^-$

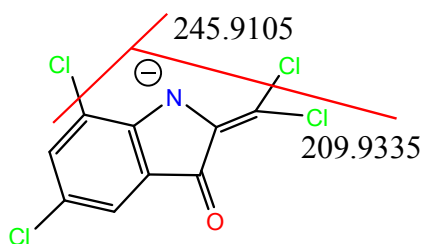
Exact Mass:  $m/z = 303.8896/305.8867/307.8837/309.8808$

226

227 **Figure S9.** Structures of parent and fragment ions for the product P5. Red lines provide the potential  
228 fragmentation cleavage points to produce fragment ions.

229

230 **Product P6:** The extract ion (279.89 or 281.89) chromatogram show the retention time (RT) of P6 at  
231 10.93 min (Figure S3f). The full-scan mass spectrum of the product P6 at RT 10.9 min exhibit  
232 molecular ion ( $[M-H]^-$ ) at  $m/z$  279.8897/281.8867/283.8838/285.8809 in the ~8:10:6:1 isotope ratio  
233 characteristic of this compound containing four chlorine (Figure 2f). High-resolution MS analysis  
234 resolved the product ion at  $m/z$  279.8897 consistent with an elemental formula of  $C_9H_2NOCl_4^-$  (exact  
235 mass  $m/z$  279.8896; mass shift 0.59 ppm). MS/MS analysis of  $m/z$  281.8867 shows the fragments at  
236  $m/z$  245.9105 and 209.9335, consistent with elemental formulas of  $C_9HNOCl_3^-$  (exact mass 245.9100;  
237 mass shift 2.16 ppm) and  $C_9NOCl_2^-$  (exact mass 209.9333; mass shift 1.01 ppm), indicating the loss  
238 of one and two HCl from the precursor ion (Figure S4f and S10). According to the results from high-  
239 resolution MS analysis, the product P6 was suggested to be 5,7-dichloro-2-  
240 (dichloromethylene)indolin-3-one, which would be formed from the product P4 via the reactions of  
241 the opening the ring of cyclohexa-dienone, chlorine electrophilic addition, decarboxylation, chlorine  
242 re-addition, water addition and small molecule disinfection byproduct  $CH_2Cl_2$  elimination (section  
243 “Proposed reaction pathway” in the manuscript).



P6: 5,7-dichloro-2-(dichloromethylene)indolin-3-one

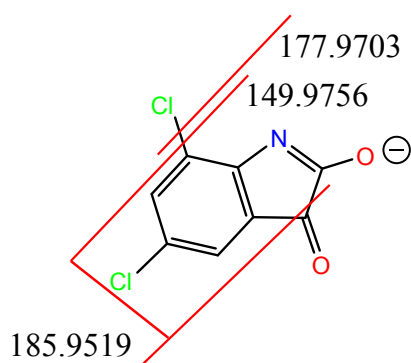
Chemical formula:  $\text{C}_9\text{H}_2\text{NOCl}_4^-$

Exact Mass:  $m/z = 279.8896/281.8866/283.8837/285.8808$

**Figure S10.** Structures of parent and fragment ions for the product P6. Red lines provide the potential fragmentation cleavage points to produce fragment ions.

**Product P7:** The extract ion (213.95) chromatogram show the retention time (RT) of P7 at 8.14 min (Figure S3g). The full-scan mass spectrum of the product P7 at RT 8.13 min exhibit molecular ion ( $[\text{M}-\text{H}]^-$ ) at  $m/z$  213.9469/215.9440/217.9410 in the ~9:6:1 isotope ratio characteristic of this compound containing two chlorine (Figure 2g). High-resolution MS analysis resolved the product ion at  $m/z$  213.9469 consistent with an elemental formula of  $\text{C}_8\text{H}_2\text{NO}_2\text{Cl}_2^-$  (exact mass  $m/z$  213.9468; mass shift 0.60 ppm). MS/MS analysis of  $m/z$  213.9469 shows the fragments at  $m/z$  185.9519, 177.9703 and 149.9756, consistent with elemental formulas of  $\text{C}_7\text{H}_2\text{NOCl}_2^-$  (exact mass 185.9519; mass shift 0 ppm),  $\text{C}_8\text{HNO}_2\text{Cl}^-$  (exact mass 177.9701; mass shift 0.96 ppm) and  $\text{C}_7\text{HNOCl}^-$  (exact mass 149.9752; mass shift 2.60 ppm), indicating the loss of the “-CO”, one HCl, and both the “-CO” and one HCl from the precursor ion (Figure S4g and S11). According to the results from high-resolution MS analysis, the product P7 was suggested to be 5,7-dichloro-2-hydroxy-3H-indol-3-one, which would be formed from the product P6 after the reactions of electrophilic addition of chlorine, nucleophilic attack of water and the small molecule disinfection byproduct  $\text{CHCl}_3$  elimination (section “Proposed reaction pathway” in the manuscript).





P7: 5,7-dichloro-2-hydroxy-3*H*-indol-3-one

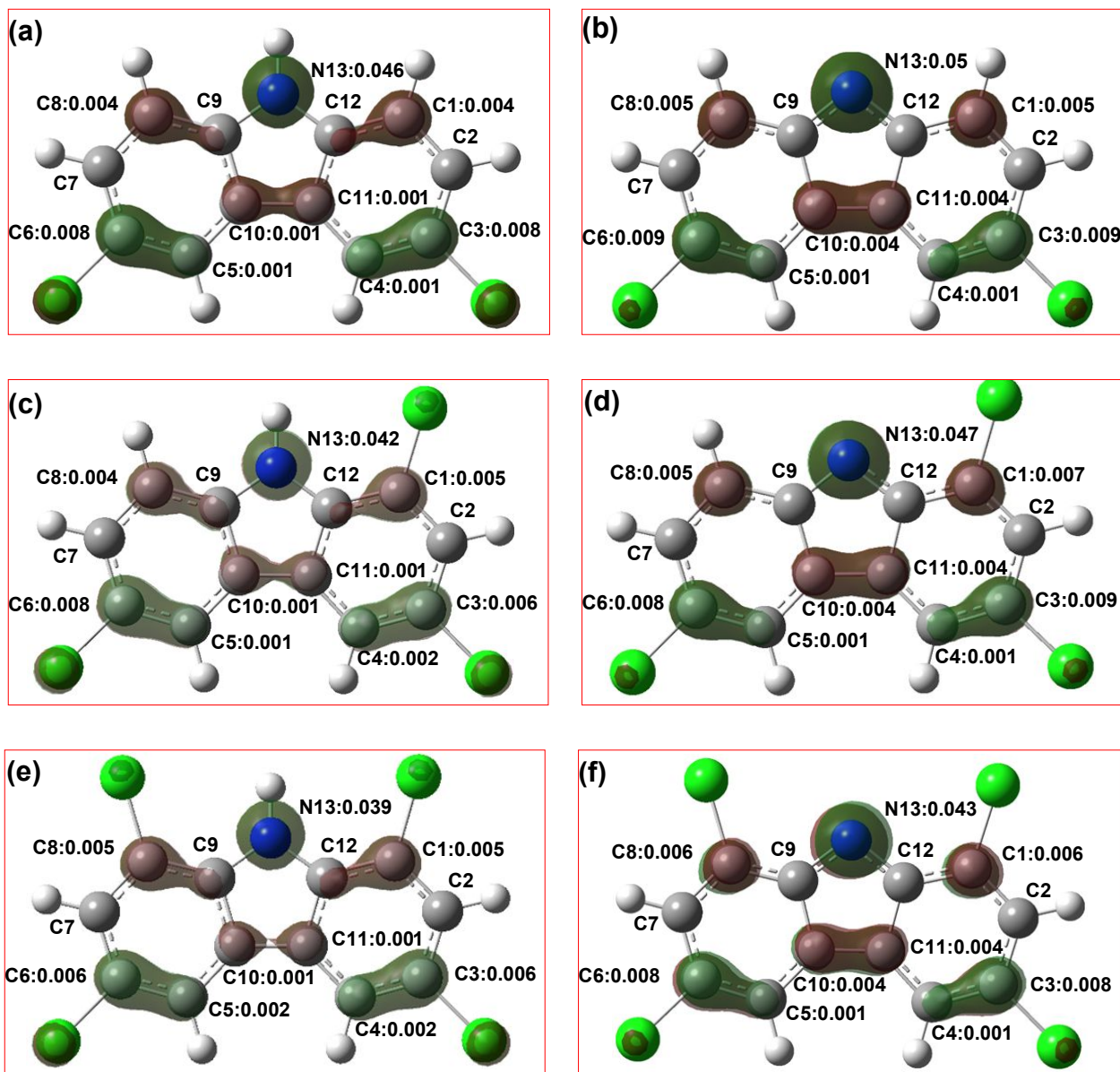
Chemical formula:  $\text{C}_8\text{H}_2\text{NO}_2\text{Cl}_2^-$

Exact Mass:  $m/z = 213.9468/215.9439/217.9409$

262

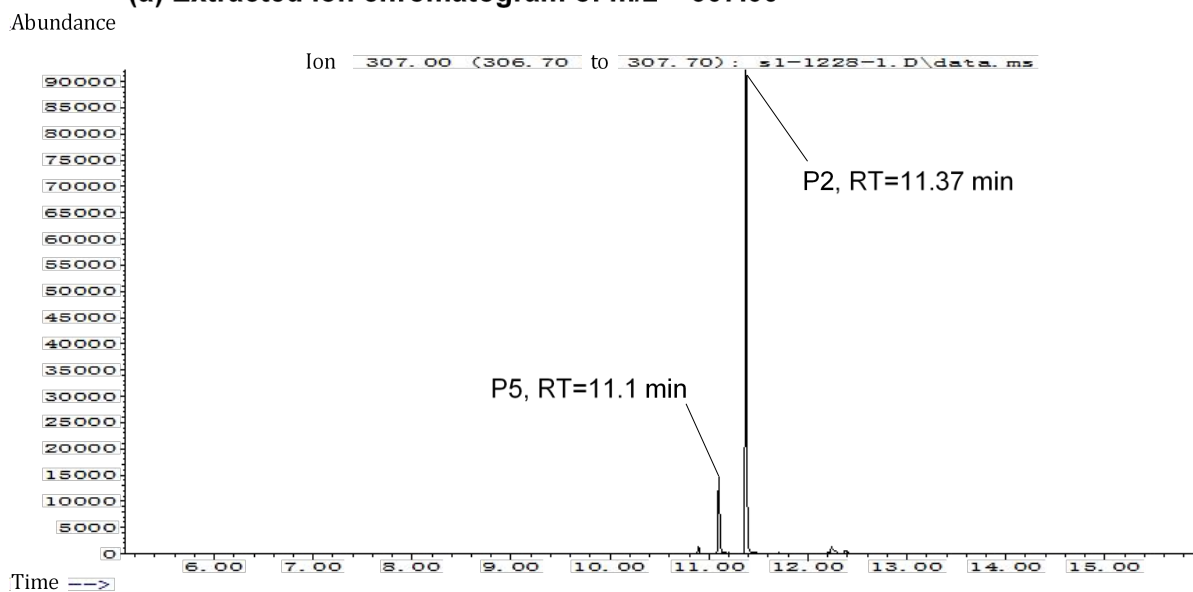
263 **Figure S11.** Structures of parent and fragment ions for the product P7. Red lines provide the potential

264 fragmentation cleavage points to produce fragment ions.

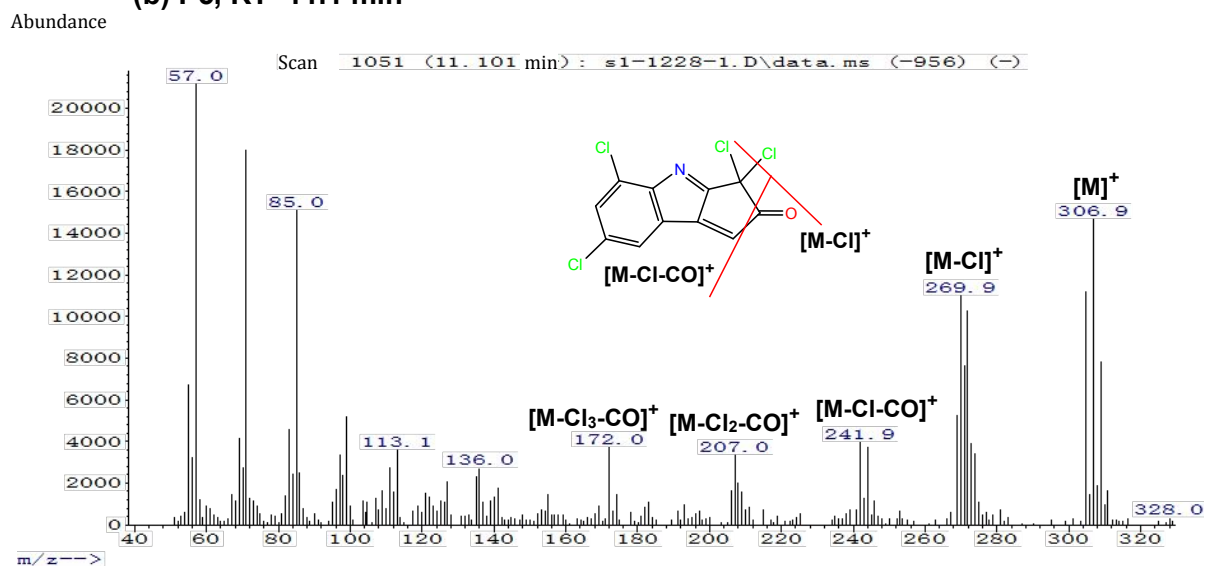


**Figure S12.** Atom HOMO (highest occupied molecular orbital) densities of (a) [36-CCZ], (b) [36-CCZ-H]<sup>-</sup>, (c) [136-CCZ], (d) [136-CCZ-H]<sup>-</sup>, (e) [1368-CCZ] and (f) [1368-CCZ-H]<sup>-</sup>. Atom HOMO densities were calculated using the DFT method with the B3LYP/6-311G\* basis set in Gaussian 09. The isosurface of HOMO (isovalue = 0.05) and the higher 2FED<sup>2</sup> HOMO values (>0.001) of the six chemicals were provided. As show in figure S12a, c and e, the 2FED<sup>2</sup> HOMO values on “N13” were decreased with the increase of the number of chlorine substituents on carbazole rings, indicating that the hydrogen atom on “-NH” becomes easy to dissociate as the number of chlorine substituents on carbazole rings increases. The dissociation of hydrogen on “-NH” in [36-CCZ] (Figures 12a), [136-CCZ] (Figures 12c) and [1368-CCZ] (Figures 12e) induces the increase of the electron cloud density of the corresponding compound [36-CCZ-H]<sup>-</sup> (Figures 12b), [136-CCZ-H]<sup>-</sup> (Figures 12d) and [1368-CCZ-H]<sup>-</sup> (Figures 12f) on the C3 and C6 positions.

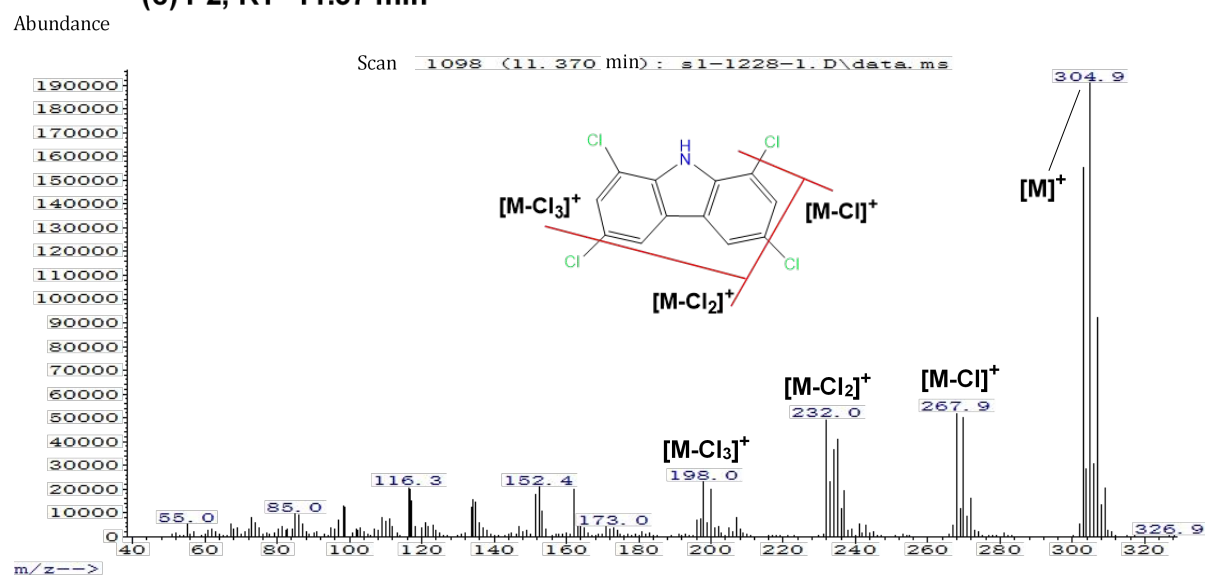
**(a) Extracted ion chromatogram of m/z = 307.00**



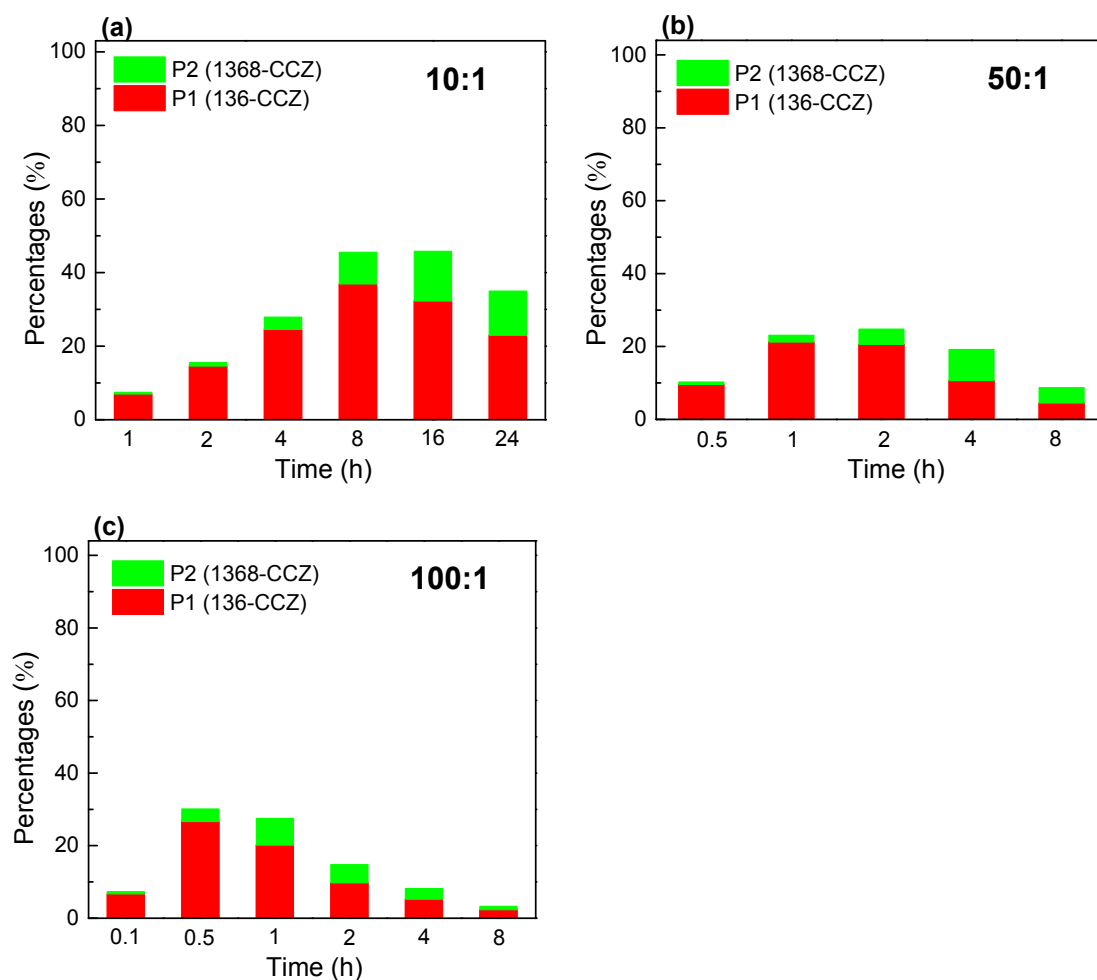
**(b) P5, RT=11.1 min**



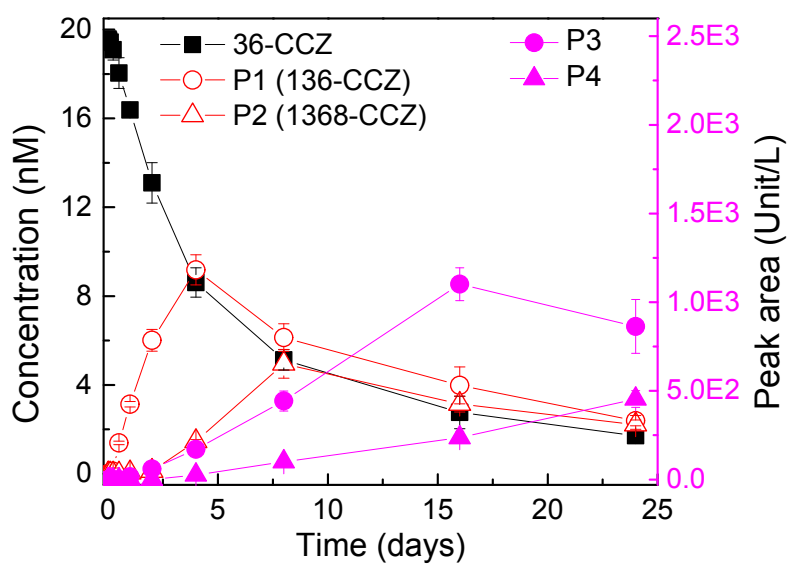
**(c) P2, RT=11.37 min**



282 **Figure S13.** Analysis of product P5 using gas chromatography coupled with mass spectrometry  
283 (GC–MS) (a) Extracted ion chromatograms of  $m/z = 307$  show approximate retention times of the  
284 detected products P5 at 11.1 min and P2 at 11.37 min in chlorinated water samples. The extracted ion  
285 chromatogram of  $m/z = 307$  has the characteristic peaks of P5 and P2 because both the products P5  
286 and P2 has the characteristic ion of  $m/z = 307$  in the mass spectra. (b) Mass spectrum of the product  
287 P5 at the retention time of 11.1 min. (c) Mass spectrum of the product P2 at the retention time of  
288 11.37 min.  
289



**Figure S14.** The percentages of the chlorination products P1 and P2 at different chlorine/36-CCZ molar ratios. The percentages of the products P1 and P2 at the chlorine/36-CCZ molar ratio of (a) 10:1, (b) 50:1, and (c) 100:1. Experimental conditions:  $[36\text{-CCZ}]_0 = 1.21 \pm 0.03 \mu\text{M}$ ,  $\text{pH} = 7.6$ , and temperature =  $20 \pm 1 \text{ }^\circ\text{C}$ .



**Figure S15.** Product evolution versus time at environmentally relevant concentration of chlorine over 24 days. Experimental conditions:  $[\text{chlorine}]_0 = 0.7 \mu\text{M}$  (0.05 mg/L),  $[\text{36-CCZ}]_0 = 20 \text{ nM}$  (4.72  $\mu\text{g/L}$ ), chlorine/36-CCZ molar ratio of 35:1, pH = 7.6 and temperature =  $20 \pm 1 \text{ }^\circ\text{C}$ .

301   **References**

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