**Table 1**. DOM properties and the second–order rate constants for the reactions of $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $^{\bullet}OH$ with DOM

| No. | Full name | Abbreviation | $M_W$[a] (Da) | E2/E3[b] | FI[c] | $SUVA_{254}$[d] (L $mg^{-1}m^{-1}$) | TAC[e] ($mgGA/mg_C$) | $k_{DOM-Cl^{\bullet}}$ ($10^8$ $M_C^{-1}$ $s^{-1}$) | $k_{DOM-Cl_2^{\bullet-}}$ ($10^7$ $M_C^{-1}$ $s^{-1}$) | $k_{DOM-^{\bullet}OH}$ ($10^8$ $M_C^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Suwannee River I NOM[f, g] | SRNOM I | 2200 | 4.45 | 1.35 | 4.36 | 0.26 | 3.71±0.34 | 1.71±0.21 | 3.0 [13] |
| 2 | Suwannee River II NOM[h] | SRNOM II | 1940[o] | 4.85 | 1.39 | 4.00 | 0.24 | 4.12±0.32 | 1.64±0.35 | |
| 3 | Nordic Lake NOM | NLNOM | 1795[o] | 4.60 | 1.44 | 4.64 | 0.33 | 4.50±0.30 | 1.31±0.17 | |
| 4 | Upper Mississippi River NOM | UMNOM | 1510 | 4.67 | 1.78 | 3.55 | 0.15 | 5.93±0.29 | 2.18±0.18 | |
| 5 | Suwannee River II FA[i] | SRFA | 2019 | 4.61 | 1.34 | 4.13 | 0.30 | 6.60±0.63 | 2.27±0.21 | 1.60±0.24 [9]<br>2.06±0.09 [18] |
| 6 | Pahokee Peat FA | PPFA | 1894 | 4.17 | 1.27 | 6.25 | 0.19 | 10.17±0.80 | 2.75±0.53 | |
| 7 | Nordic Lake FA | NLFA | 1698[o] | 4.28 | 1.41 | 4.44 | 0.34 | 10.38±1.02 | 2.93±0.36 | |
| 8 | Pony Lake FA | PLFA | 1517 | 5.00 | 1.55 | 2.52 | 0.29 | 7.40±0.78 | 0.99±0.10 | 6.9±0.53 [18] |
| 9 | Pahokee Peat HA[j] | PPHA | 2977 | 2.81 | 0.89 | 6.90 | 0.31 | 4.26±0.42 | 2.61±0.48 | |
| 10 | Leonardite HA | LHA | 3320[o] | 2.54 | 1.24 | 5.72 | 0.39 | 5.20±0.27 | 3.57±0.53 | |
| 11 | Elliott Soil IV HA | ESHA | 3089 | 2.33 | 0.84 | 6.51 | 0.21 | 5.30±0.49 | 2.80±0.61 | 1.21±0.09 [18] |
| 12 | Salt River HPOA[k] | SR–HPOA | 1584 | 4.84 | 1.33 | 2.75 | 0.13 | 9.85±0.45 | 0.61±0.11 | |
| 13 | Salt River HPON[l] | SR–HPON | 1023 | 5.49 | 1.21 | 1.88 | 0.07 | 11.20±0.64 | 0.75±0.13 | |
| 14 | Salt River TPIA[m] | SR–TPIA | 980[o] | 6.31 | 1.46 | 2.13 | 0.11 | 12.60±1.15 | 0.82±0.12 | |
| 15 | Salt River TPIN[n] | SR–TPIN | 892[o] | 6.82 | 1.62 | 2.01 | 0.09 | 15.17±1.56 | 0.98±0.10 | |
| 16 | Saguaro Lake HPOA | SL–HPOA | 1258 | 9.70 | 1.89 | 2.42 | 0.06 | 5.64±0.33 | 0.46±0.09 | 1.73±0.04 [9] |
| 17 | Saguaro Lake TPIA | SL–TPIA | 1104[o] | 7.23 | 1.52 | 2.06 | 0.08 | 8.30±0.40 | 0.65±0.12 | 1.45±0.02 [9] |
| 18 | Nogales WWTP HPOA | WWTP–HPOA | 1376 | 5.52 | 1.87 | 1.12 | 0.13 | 8.42±0.51 | 1.55±0.29 | |
| 19 | Nogales WWTP TPIA | WWTP–TPIA | 992 | 8.20 | 2.39 | 1.29 | 0.13 | 13.05±0.89 | 1.37±0.12 | 3.63±0.31[9] |
| **Averages** | | | **1746** | **5.18** | **1.46** | **3.61** | **0.20** | **7.99±0.61** | **1.68±0.25** | **2.5 [17]** |

a: Mw=weight averaged molecular weight. b: E2/E3=absorbance at 254 nm divided by absorbance at 365 nm. c: FI= fluorescence index. d: $SUVA_{254}$=specific UV absorbance at 254 nm. e: TAC=total antioxidant capacity, GA=gallic acid. f: NOM=natural organic matter. g: 1R101N. h: 2R101N i: FA=fulvic acid. j: HA=humic acid. k: HPOA=hydrophobic acid. l: HPON=hydrophobic neutral. m: TPIA= Transphilic acid. n: TPIN=Transphilic neutral. o: estimated from the established correlation between $M_W$ and $SUVA_{280}$ for aquatic NOM sample[22]

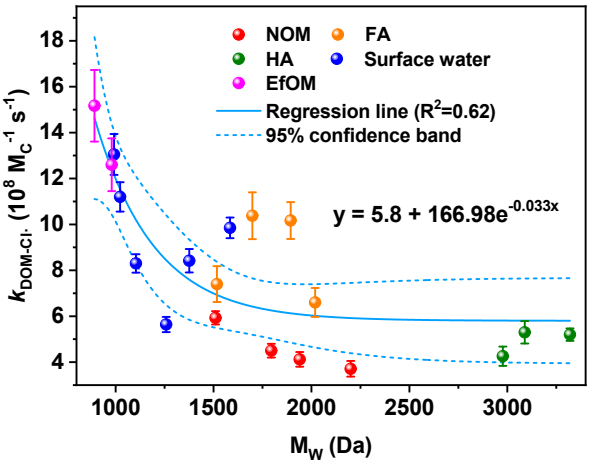


**Figure 1.** The relationships between weight-averaged molecular weight ($M_W$) and the second-order reaction rate constants of $Cl^{\bullet}$ with DOM isolates ($k_{DOM-Cl\bullet}$) with the regression line and 95% confidence interval for the regression. Red dots: NOM, orange dots: FA, olive dots: HA, blue dots: surface waters, magenta dots: EfOM.

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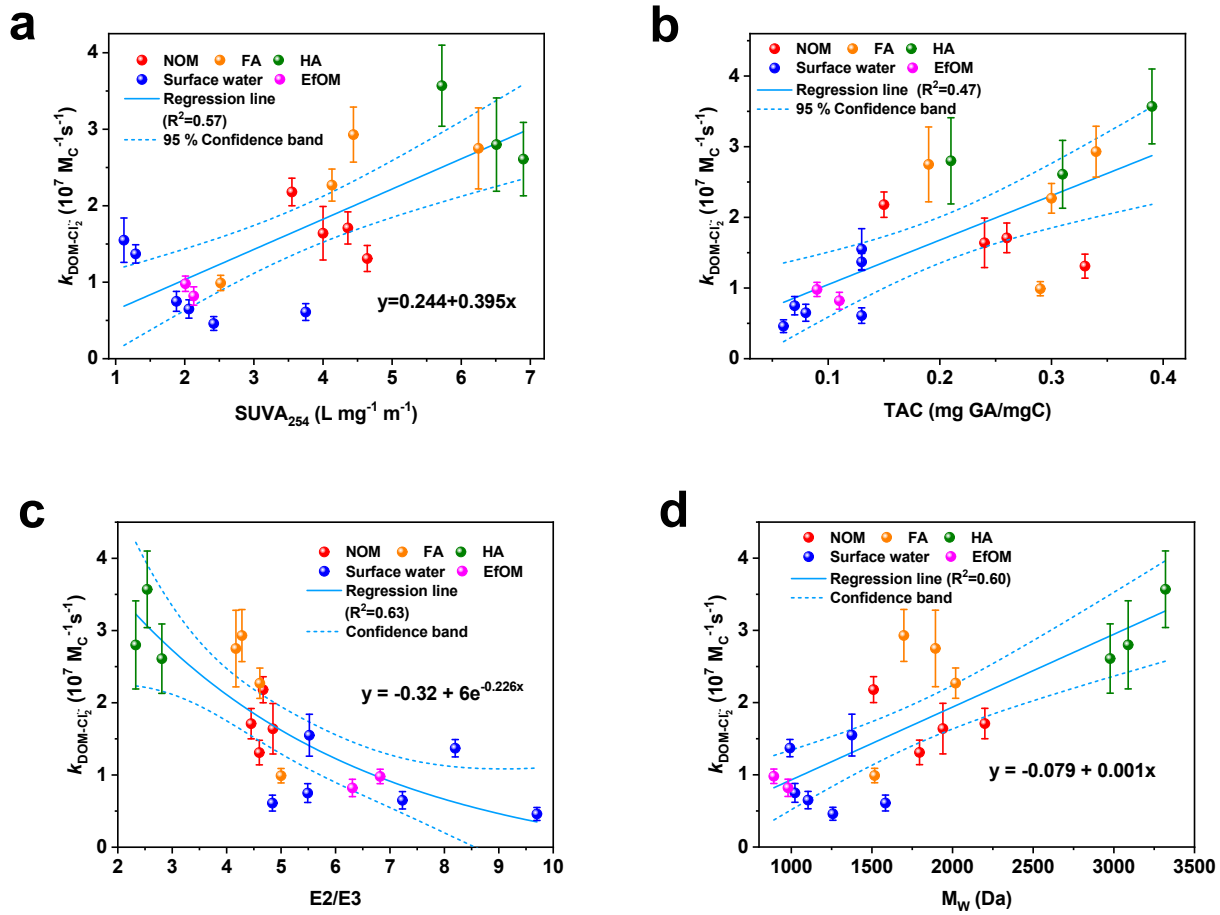


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622 **Figure 2.** Relationships between $Cl_2^{\bullet-}$ reaction rate constants ($k_{DOM-Cl_2\bullet-}$) and different DOM
623 properties (a) $SUVA_{254}$, (b) TAC, (c) E2/E3 and (d) $M_W$ with the regression line and 95% confidence
624 interval for the regression. Red dots: NOM, orange dots: FA, olive dots: HA, blue dots: surface
625 waters, magenta dots: EfOM.

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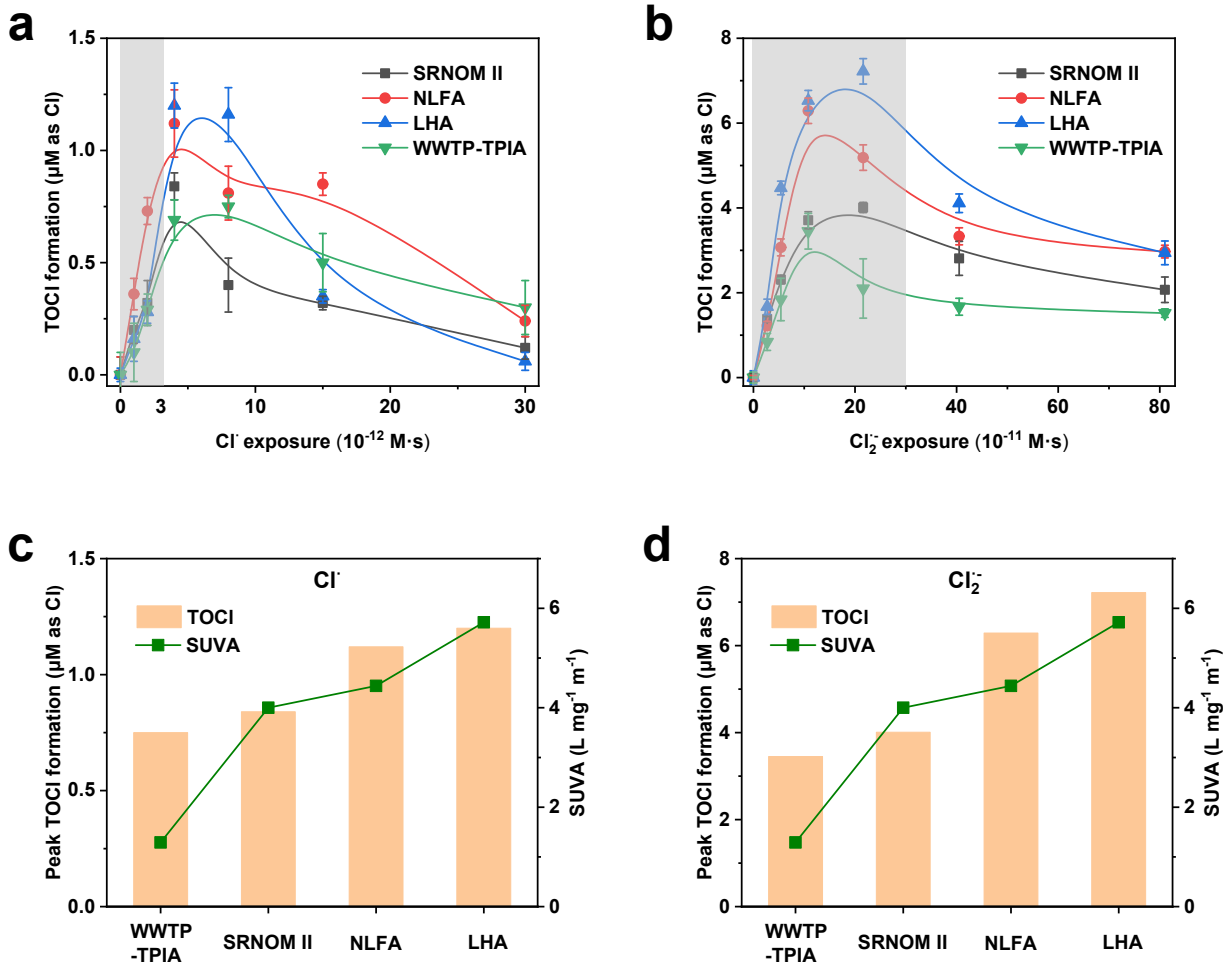


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629 **Figure 3.** (a-b) The evolution profiles of TOCl concentrations with (a) $Cl^{\bullet}$ oxidant exposure and (b)

630 $Cl_2^{\bullet-}$ oxidant exposure. Conditions: [DOM]=2.5 $mg_C$ $L^{-1}$, pH=7.0. The grey areas represent typical

631 $Cl^{\bullet}$ exposure ($3\times10^{-15}$–$3\times10^{-12}$ M·s) and $Cl_2^{\bullet-}$ exposure ($3\times10^{-13}$–$3\times10^{-10}$ M·s) in typical UV-based

632 AOPs. (c-d) The dependence of peak TOCl concentrations formed from DOM reactions with (c) $Cl^{\bullet}$

633 and (d) $Cl_2^{\bullet-}$ vs. SUVA.

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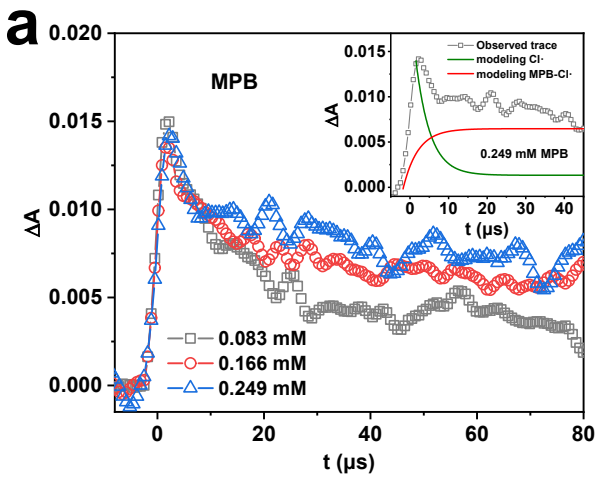


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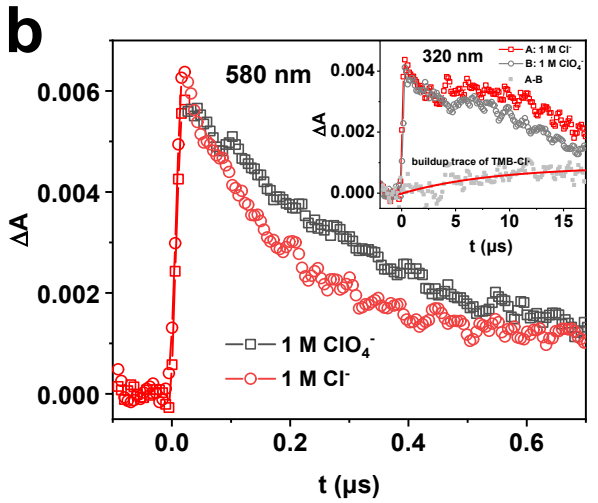


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637 **Figure 4.** (a) Kinetic traces at 320 nm for methylparaben (MPB) reacting with Cl•. Inset: modeling
638 curve of Cl• and MPB−Cl• adduct. (b) The decay kinetic traces of 1,3,5-trimethoxybenzene's (TMB)
639 cation radical ($TMB^{\bullet+}$) at 1 M $Cl^-$ and 1 M $ClO_4^-$. Inset: kinetic traces at 320 nm at 1 M $Cl^-$ and 1 M
640 $ClO_4^-$ and modeling buildup trace of TMB−Cl• adduct. $ClO_4^-$ was used for ionic strength control.

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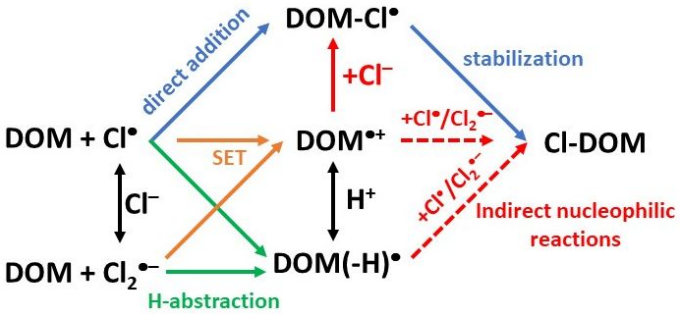


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643 **Scheme 1.** Proposed formation mechanism of chlorinated products from DOM reacting with $Cl^{\bullet}$ or
644 $Cl_2^{\bullet-}$. Blue and red arrows represent direct addition and indirect nucleophilic reactions, respectively.
645 SET represents single electron transfer mechanism. Dashed arrows represent speculative pathways
646 from literature.