

1 Supporting Information for:

2 Role of Tertiary Amines in Enhancing Trihalomethane and  
3 Haloacetic Acid Formation During Chlorination of Aromatic  
4 Compounds and a Natural Organic Matter Extract

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17 19 Pages

18 2 Text Sections

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24 **Text S1. Tertiary Amine Measurements**

25 Additional experiments were performed to evaluate if the quenching agent, ascorbic acid,  
26 added prior to tertiary amine analysis potentially affected the measured tertiary amine values.  
27 This was of concern since ascorbic acid was added to reduce the residual free chlorine in the  
28 experimental samples, but it was unclear if the chlorammonium intermediate ( $R_3N-Cl^+$ ) formed  
29 during these reactions could also be reduced back to its parent tertiary amine. This would then  
30 alter how the amine measurements were defined such that these values could potentially  
31 represent the concentration for only the residual amine or also include  $R_3N-Cl^+$  as well. In order  
32 to evaluate this effect, MES was chosen as a representative tertiary amine to be first exposed to  
33 free chlorine over time, and then either not quenched or periodically quenched with excess (i)  
34 ascorbic acid, (ii) RES, or (iii) both RES and SA. The MES concentration in these samples were  
35 then immediately measured and were plotted in Fig. S1. In addition, the predicted MES  
36 concentration was also plotted in Fig. S1 by simulating its kinetic degradation during  
37 chlorination using Kintecus<sup>1</sup> (equations used in this model simulation provided in Table S2).

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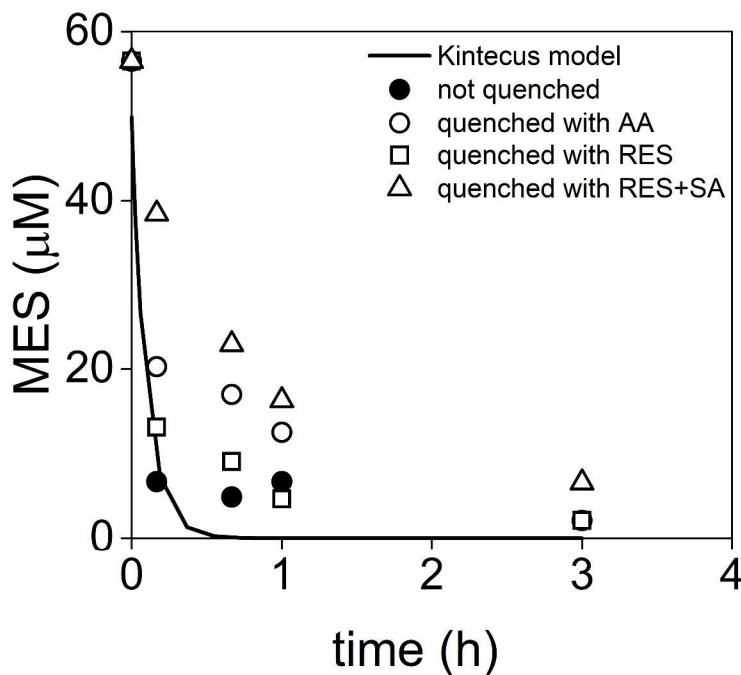
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**Figure S1.** The measured residual MES concentration following exposure to free chlorine after not quenching or quenching with either ascorbic acid (AA) ( $2 \times [\text{free chlorine}]_0$ ), RES (3mM), or both RES (3mM) and SA (3mM). The model curve represents the predicted MES degradation in the presence of free chlorine ( $[\text{MES}]_0 = 50 \mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$ ; pH 7.1-7.2;)

The results first indicated a fairly close overlap between the unquenched samples and the model curve, which implied that the analytical technique used to quantify MES in these sample matrices was sound and no artifactual formation occurred. Second, it appeared that all three quenching techniques exhibited an increase in the MES concentration as compared to the unquenched values/model curve. For example, at 10 min, the MES concentrations for ascorbic acid, RES, and RES + SA were 2.8, 1.8, and 5.3 times higher than the model curve values (Fig. S1). This trend was followed through over 3 h, and it indicated that the greatest increase in MES for the three quenching techniques followed in the order of RES+SA > ascorbic acid > RES (Fig. S1). Such a pattern demonstrated that these quenching techniques, and especially ascorbic acid, did appear to have some effect on reducing the formed intermediate,  $\text{MES-Cl}^+$ , back to MES.

72 The extent of how much was reformed though remained unclear since these  $R_3N-Cl^+$   
73 intermediates can potentially undergo elimination and degrade to other by-products as well (see  
74 later discussions and Scheme 1 in main text).

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76 **Text S2.** Residual Free Chlorine Measurements.

77 Additional experiments were conducted to determine if the residual free chlorine  
78 measurements taken for samples that also contained tertiary amines reflected only the total free  
79 chlorine ( $[HOCl] + [OCl^-]$ ) or also included other chlorinating agents (e.g.,  $R_3N-Cl^+$ ). These  
80 experiments were performed by exposing 25  $\mu M$  free chlorine to MES or TMA ( $[TMA \text{ or}$   
81  $MES]_0/[free \text{ chlorine}]_0 = 2$ ) for 44 or 30 min, respectively. These exposure times were selected  
82 since they were predicted to yield 95% conversion from the reactants to the respective  
83 chlorammonium species, which was determined by performing model simulations with Kintecus  
84 <sup>®</sup><sup>1</sup> (see Table 1 for rate constants used and Table S2 for the model reactions and conditions  
85 used). Samples were then quenched with DPD and measured for their absorbance at 515 nm. The  
86 results indicated that at these times, the absorbance readings were less than 0.01, which proved  
87 that the  $R_3N-Cl^+$  generated did not react with DPD. These results were expected because  $R_3N-$   
88  $Cl^+$  is only expected to participate in electrophilic substitution reactions rather than be involved  
89 in oxidation reactions. However, DPD must be oxidized through a one electron transfer reaction  
90 in order to form the Würster dye (pink dye which elicits a colorimetric response).<sup>2</sup> Therefore, the  
91 DPD method was found to only quantify the residual free chlorine concentration without  
92 interference from the  $R_3N-Cl^+$  generated during these reactions.

93 **Table S1.** The compound names, formula, molecular weights (MW), retention times (RT), parent and product masses, fragmentor  
 94 voltages (FV), collision energies (CE), cell accelerator voltages (CAV), and source parameters (DGT, DGF, capillary and nebulizer)  
 95 for LC/MS/MS analyses of HAAs and LC/MS analysis of MES.

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Compound	Formula	MW (g/mole)	RT	Parent	Product	FV	CE	CAV	DGT	DGF	Capillary	Nebulizer
MCAA	CH <sub>2</sub> ClCOOH	94.49	9.16	92.97	35.2	40	5	6	350	13	2500	40
MBAA	CH <sub>2</sub> BrCOOH	138.95	9.39	136.92	78.9	55	13	2	350	10	4000	35
DCAA	CHCl <sub>2</sub> COOH	128.94	11.59	126.93	82.9	60	5	6	350	13	2500	40
BCAA	CHBrClCOOH	173.39	11.96	170.88	126.8	60	5	4	300	10	4000	40
DBAA	CHBr <sub>2</sub> COOH	217.84	12.32	214.83	170.7	55	9	2	350	10	4500	35
TCAA	CCl <sub>3</sub> COOH	163.39	16.6	160.89	116.9	50	5	2	260	10	2500	40
BDCAA	CHBrCl <sub>2</sub> COOH	207.84	18	160.85	78.9	55	9	2	290	10	5000	25
CDBAA	CHBr <sub>2</sub> ClCOOH	252.29	20.7	204.8	78.9	55	9	2	260	10	4500	35
TBAA	CBr <sub>3</sub> COOH	296.74	23.3	248.75	118.9	90	17	4	320	10	4500	30
MES	C <sub>6</sub> H <sub>13</sub> NO <sub>4</sub> S	195.20	10.7	194.1		110		2	350	13	4000	40

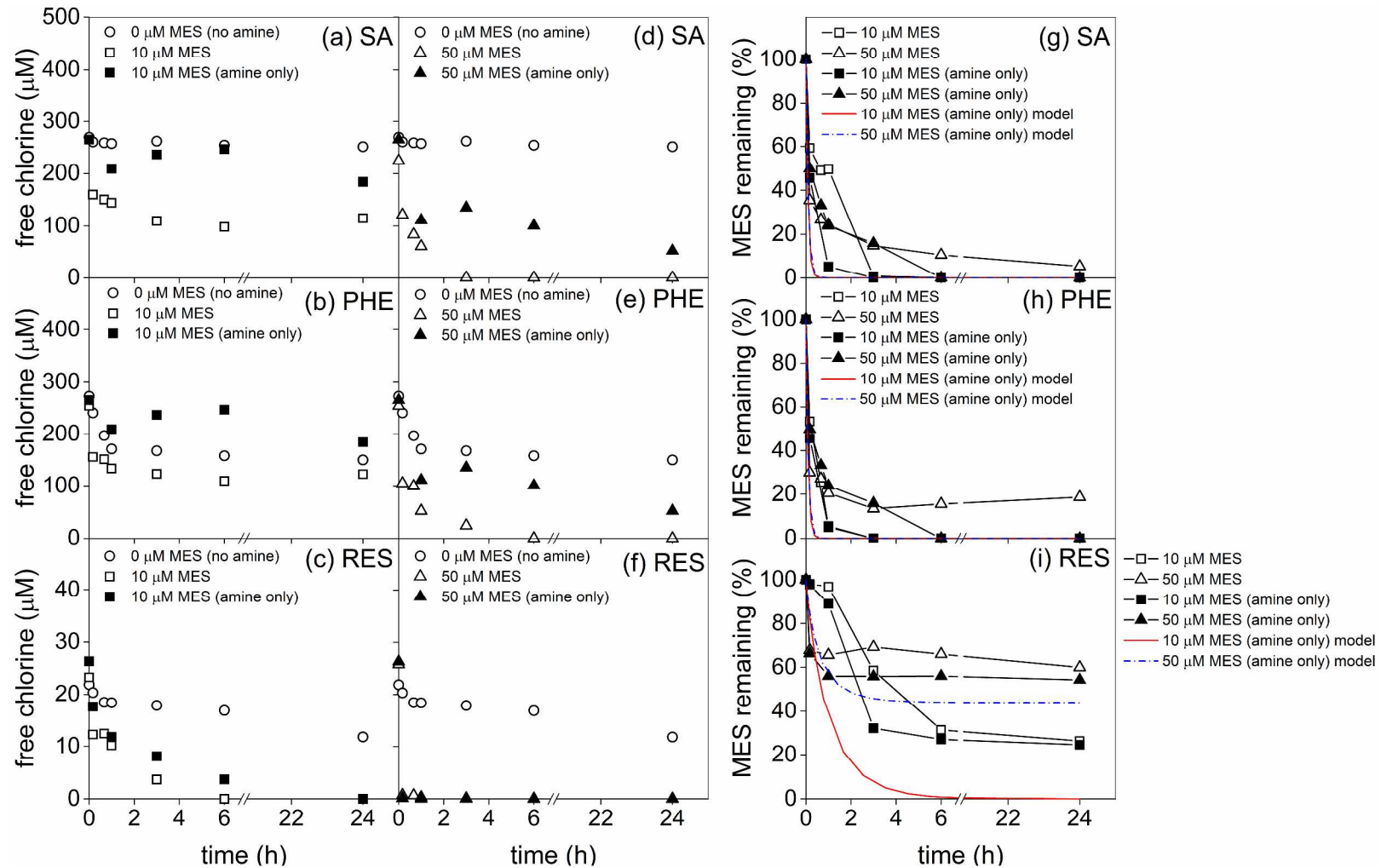
97 **Table S2.** A description of the reactions and conditions used to model the kinetics of the MES  
 98 reaction with free chlorine. A similar method was used assess the model kinetics for other  
 99 tertiary amines including TMA and TBA.

k (M <sup>-1</sup> s <sup>-1</sup> )	Reaction	Comments
3.34E+08	HOCl ==> OCl <sup>-</sup> <sup>a</sup>	hypochlorite acid dissociation, pK <sub>a</sub> = 7.45 <sup>3</sup>
6.66E+08	OCl <sup>-</sup> ==> HOCl <sup>a</sup>	hypochlorite acid dissociation
9.26E+08	MESH <sup>+</sup> ==> MES <sup>a</sup>	MES dissociation, pK <sub>a</sub> = 6.1 <sup>4</sup>
7.36E+07	MES ==> MESH <sup>+</sup> <sup>a</sup>	MES dissociation
1.83E+01	MES + HOCl ==> MES-Cl <sup>+</sup> + OH <sup>-</sup>	MES reaction with HOCl <sup>5</sup>

100 <sup>a</sup> These reaction rates were estimated by assuming k<sub>f</sub>/k<sub>b</sub> is equal to [OCl<sup>-</sup>]/[HOCl] which is  
 101 0.33×10<sup>9</sup>/0.67×10<sup>9</sup>. This value represents the ratio between the two acid-base species at pH 7.2.  
 102 These values were also multiplied by 10<sup>9</sup> in order to represent the fast equilibrium reached by  
 103 these acid-base reactions.

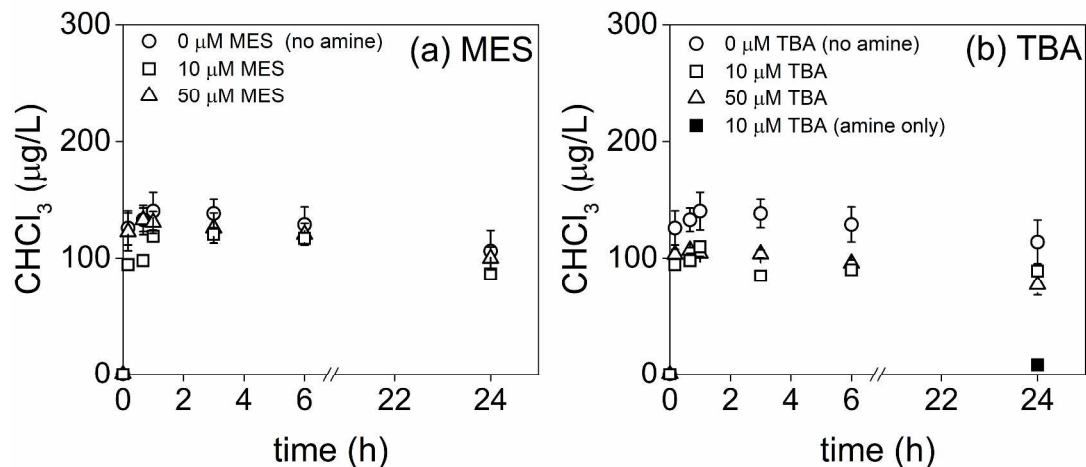
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107 **Figure S2.** Effect of MES on (a – f) the residual free chlorine and (g – i) MES % remaining over 24 h during chlorination of SA, PHE  
 108 and RES in the presence of 10 or 50 μM MES ( $[SA \text{ and PHE}]_0 = 10 \mu\text{M}$ ;  $[RES]_0 = 1 \mu\text{M}$ ;  $[MES]_0 = 0, 10 \text{ and } 50 \mu\text{M}$ ;  $[\text{free chlorine}]_0$   
 109  $= 280 \mu\text{M}$  (19.9 mg/L-Cl<sub>2</sub>) for SA and PHE, or 28 μM (2.0 mg/L- Cl<sub>2</sub>) for RES; pH 7.1-7.2).

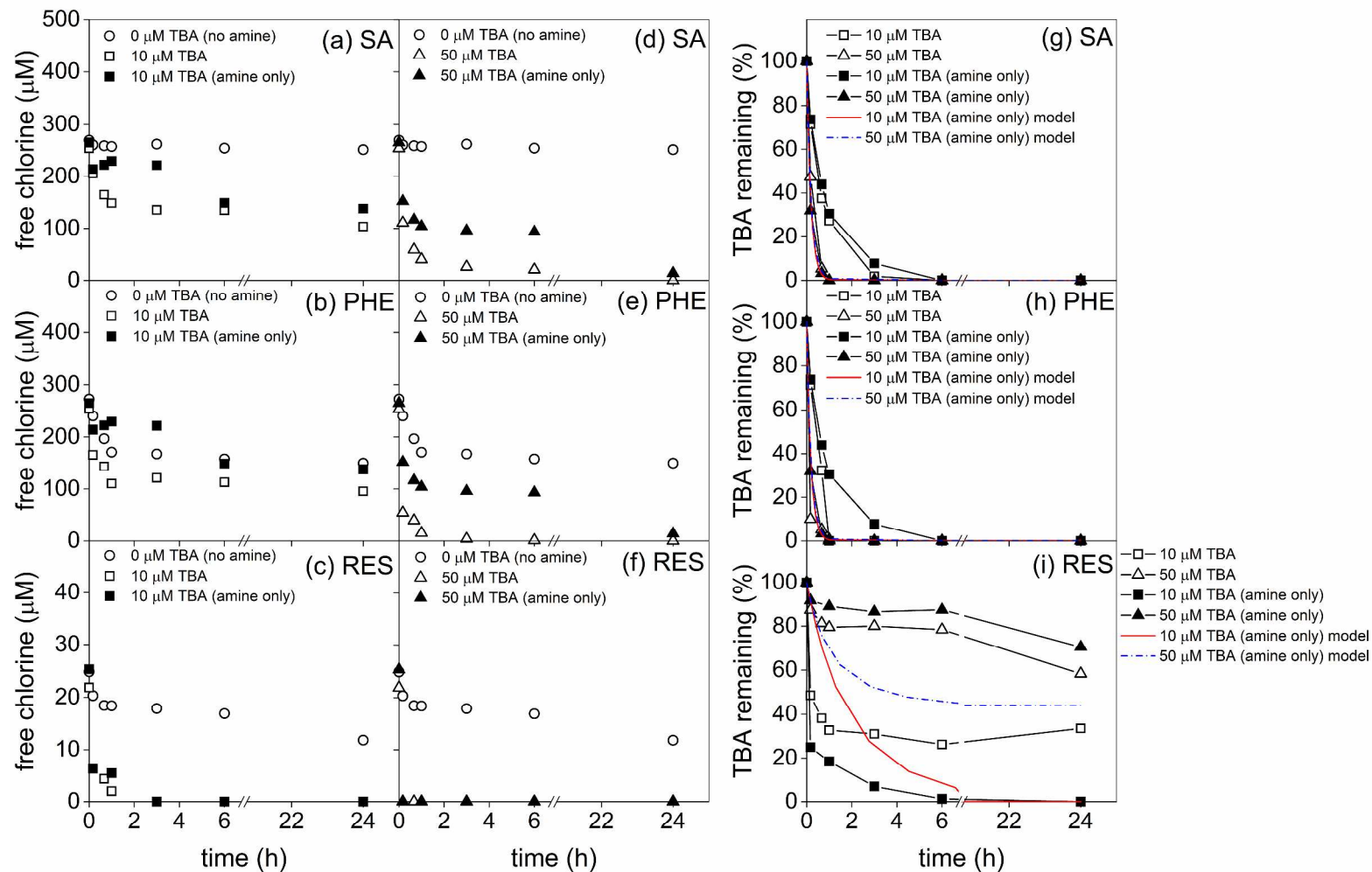


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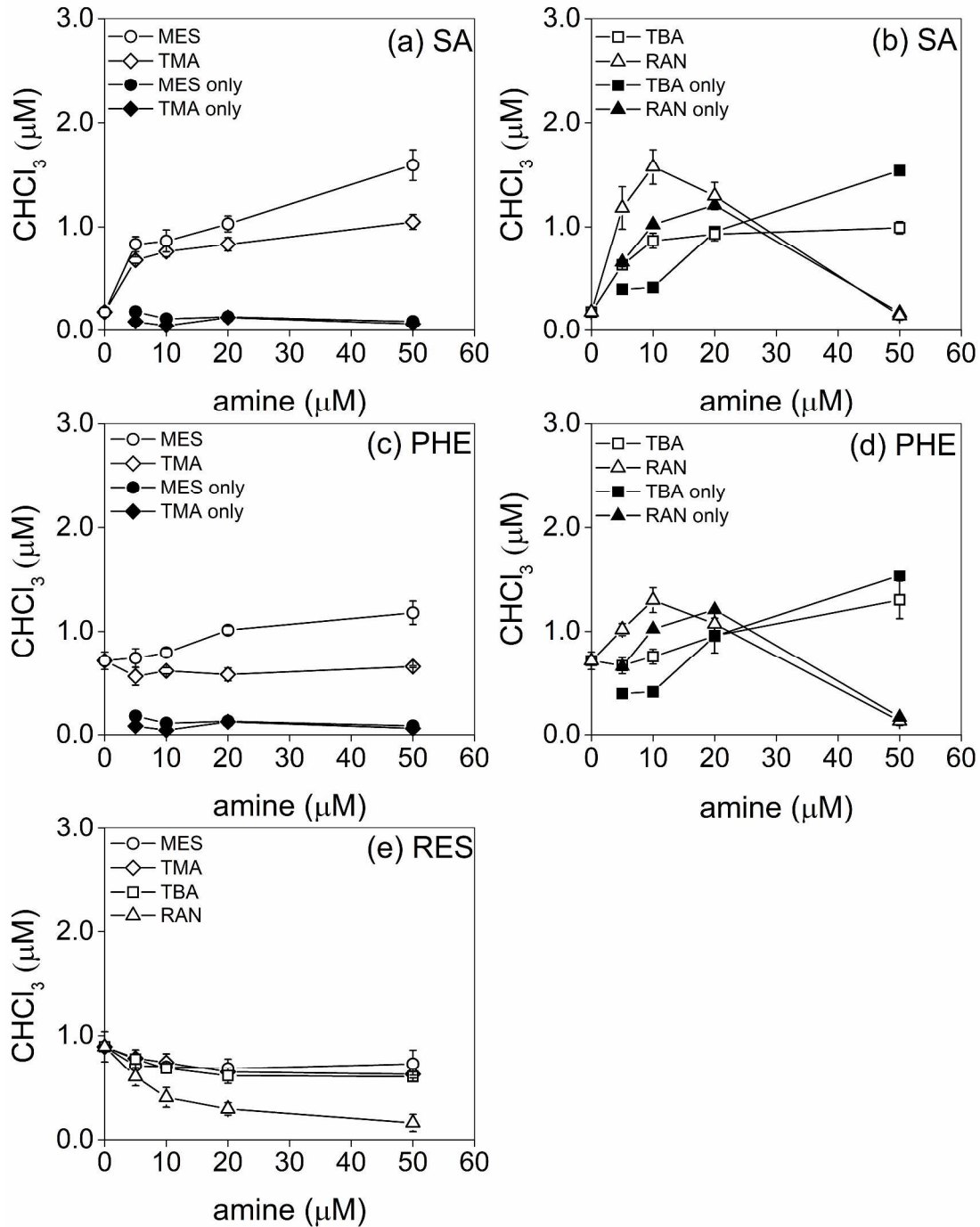
112 **Figure S3.** Effect of (a) MES and (b) TBA on  $\text{CHCl}_3$  formation over 24 h during  
 113 chlorination of RES ( $[\text{RES}]_0 = 1 \mu\text{M}$ ;  $[\text{MES or TBA}]_0 = 0, 10 \text{ and } 50 \mu\text{M}$ ;  $[\text{free chlorine}]_0 =$   
 114  $28 \mu\text{M}$  ( $2.0 \text{ mg/L- Cl}_2$ ); pH 7.1-7.2). Error bars represent the standard deviation of  $\geq 3$   
 115 replicates.





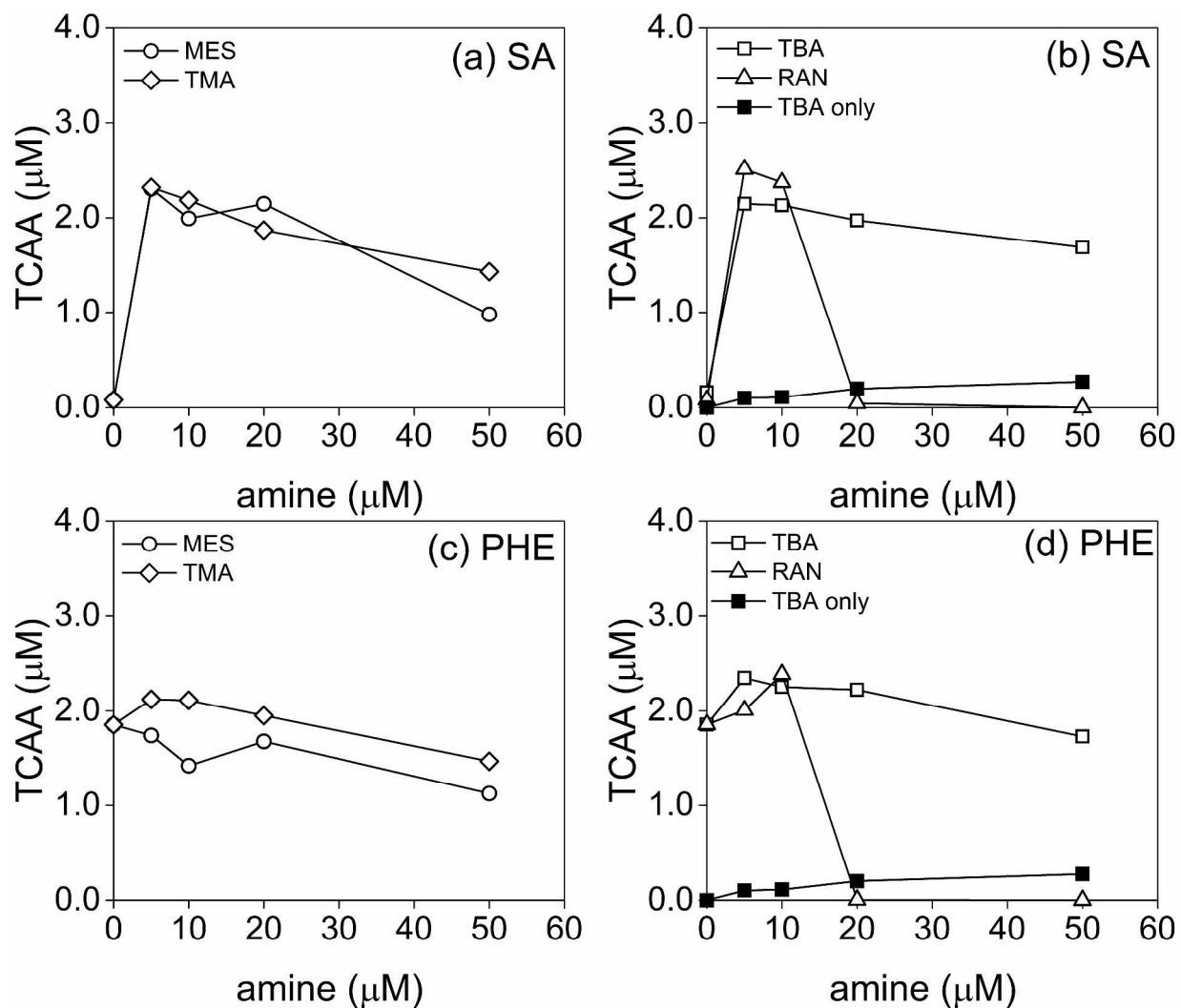
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117 **Figure S4.** Effect of TBA on (a – f) the residual free chlorine and (g – i) TBA % remaining over 24 h during chlorination of SA, PHE  
 118 and RES in the presence of TBA ( $[SA \text{ and PHE}]_0 = 10 \mu\text{M}$ ;  $[RES]_0 = 1 \mu\text{M}$ ;  $[TBA]_0 = 0, 10 \text{ and } 50 \mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$   
 119 ( $19.9 \text{ mg/L-Cl}_2$ ) for SA and PHE, or  $28 \mu\text{M}$  ( $2.0 \text{ mg/L-Cl}_2$ ) for RES; pH 7.1-7.2)



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121 **Figure S5.** Effect of amine dose (0 - 50  $\mu\text{M}$ ) on  $\text{CHCl}_3$  formation from (a, b) SA (c, d) PHE and  
 122 (e) RES) when exposed to MES, TMA, TBA or RAN after 24 h of chlorination ( $[\text{SA and PHE}]_0$   
 123 = 10  $\mu\text{M}$ ;  $[\text{RES}]_0$  = 1  $\mu\text{M}$ ;  $[\text{free chlorine}]_0$  = 280  $\mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ) for SA and PHE, or 28  $\mu\text{M}$   
 124 (2.0 mg/L-  $\text{Cl}_2$ ) for RES; pH 7.1-7.2), Error bars represent the standard deviation of  $\geq 3$   
 125 replicates.



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127 **Figure S6.** Effect of amine dose (0 - 50  $\mu\text{M}$ ) on TCAA formation from (a, b) SA (c, d) PHE  
 128 when exposed to MES, TMA, TBA or RAN after 24 h of chlorination ( $[\text{SA and PHE}]_0 = 10 \mu\text{M}$ ;  
 129  $[\text{RES}]_0 = 1 \mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ) for SA and PHE, or 28  $\mu\text{M}$  (2.0  
 130 mg/L-  $\text{Cl}_2$ ) for RES; pH 7.1-7.2).

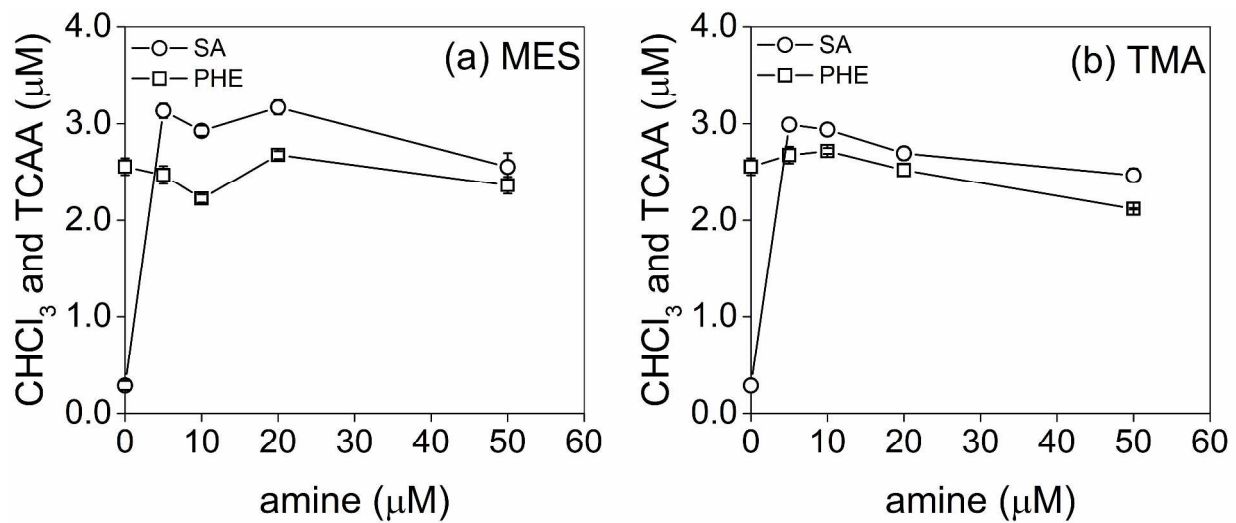
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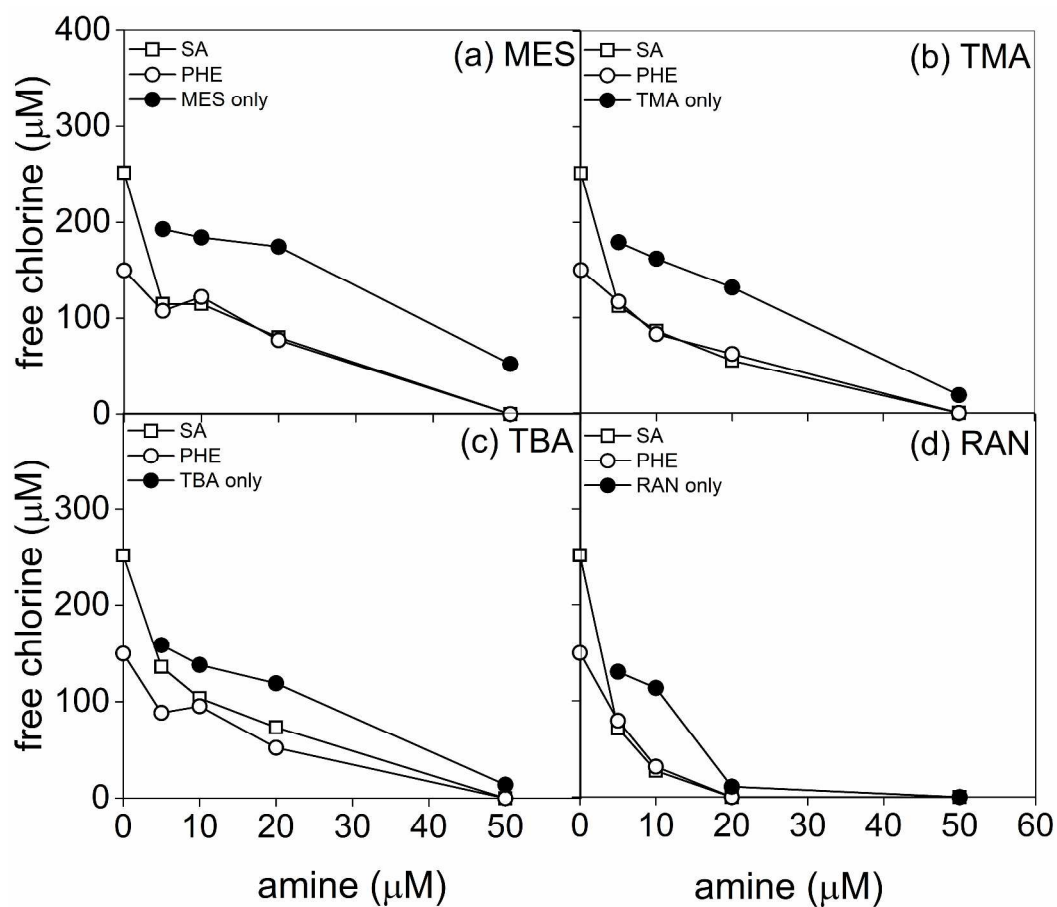
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137 **Figure S7.** Effect of amine dose (0 - 50  $\mu\text{M}$ ) on summed formation of  $\text{CHCl}_3$  and TCAA from  
 138 SA and PHE when exposed to (a) MES or (b) TMA after 24 h of chlorination ( $[\text{SA and PHE}]_0 =$   
 139 10  $\mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ); pH 7.1-7.2), Error bars represent the  
 140 standard deviation of  $\geq 3$  replicates.

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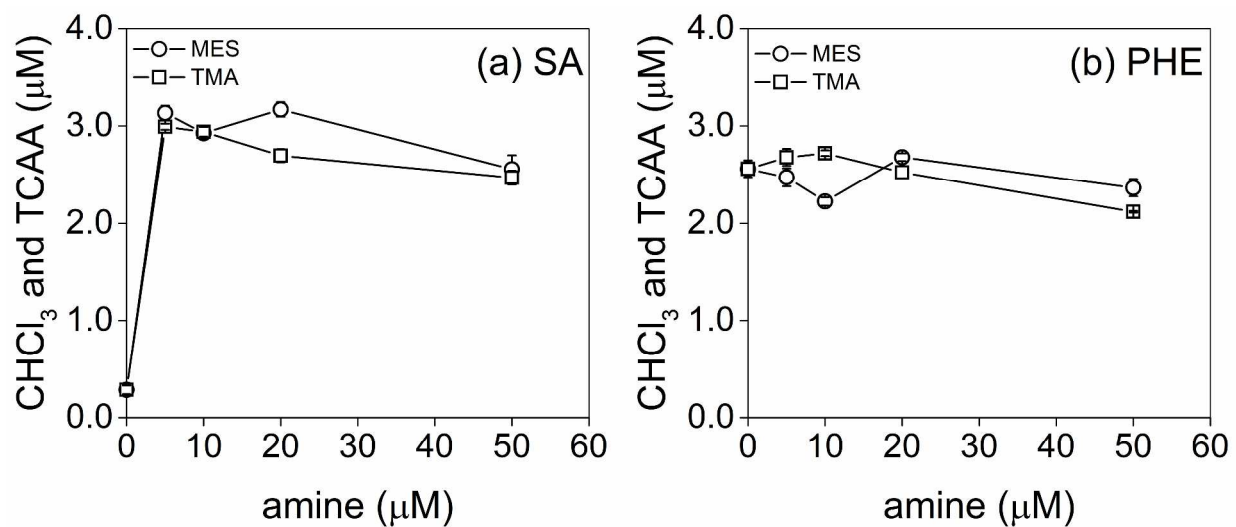


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143 **Figure S8.** Differences in residual free chlorine when SA or PHE was exposed to 5 – 50  $\mu\text{M}$  of  
 144 (a) MES (b) TMA (c) TBA (d) RAN after 24 h of chlorination ( $[\text{SA and PHE}]_0 = 10 \mu\text{M}$ ;  $[\text{free}$   
 145  $\text{chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ); pH 7.1-7.2).

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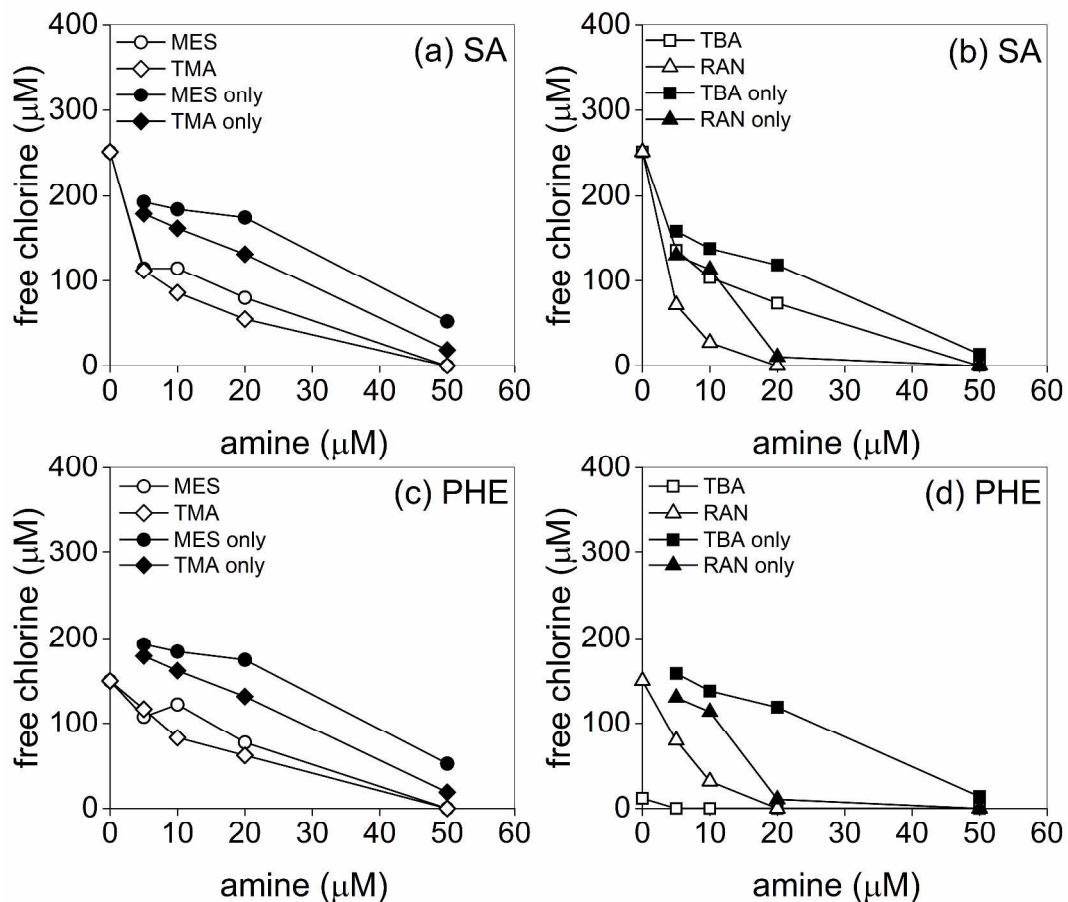


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150 **Figure S9.** Effect of amine dose (0 - 50  $\mu\text{M}$ ) on summed formation of  $\text{CHCl}_3$  and TCAA from (a)  
 151 SA and (b) PHE when exposed to MES or TMA after 24 h of chlorination ( $[\text{SA and PHE}]_0 = 10$   
 152  $\mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ); pH 7.1-7.2), Error bars represent the standard  
 153 deviation of  $\geq 3$  replicates.

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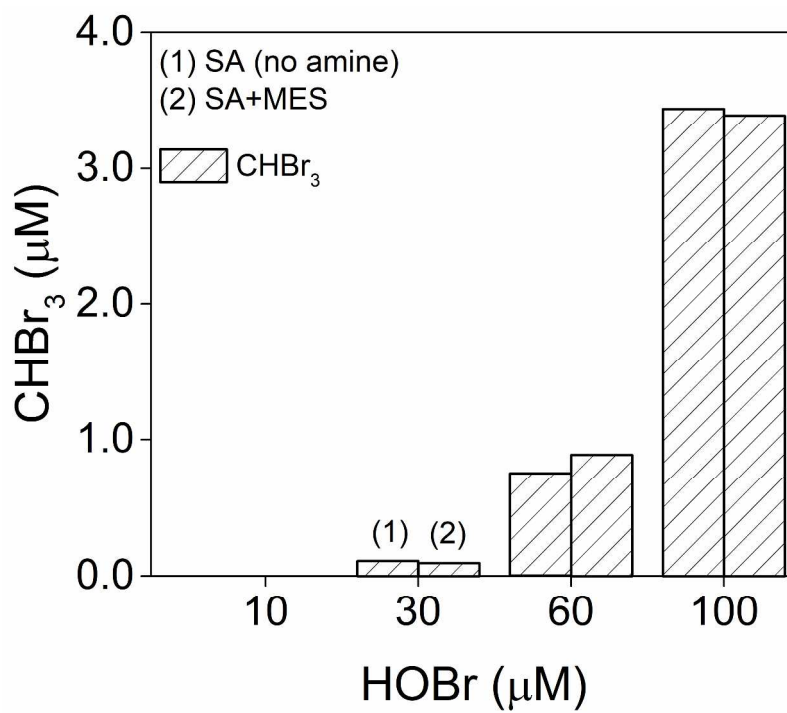


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156 **Figure S10.** Differences in residual free chlorine when (a, b) SA or (c, d) PHE was exposed to 5  
 157 – 50 μM of MES, TMA, TBA or RAN after 24 h of chlorination ( $[SA \text{ and } PHE]_0 = 10 \mu\text{M}$ ;  $[\text{free}$   
 158  $\text{chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L-Cl<sub>2</sub>); pH 7.1-7.2). RES-related data not plotted because residual  
 159 free chlorine was < d.l. for all RES/TA/FC experiments.

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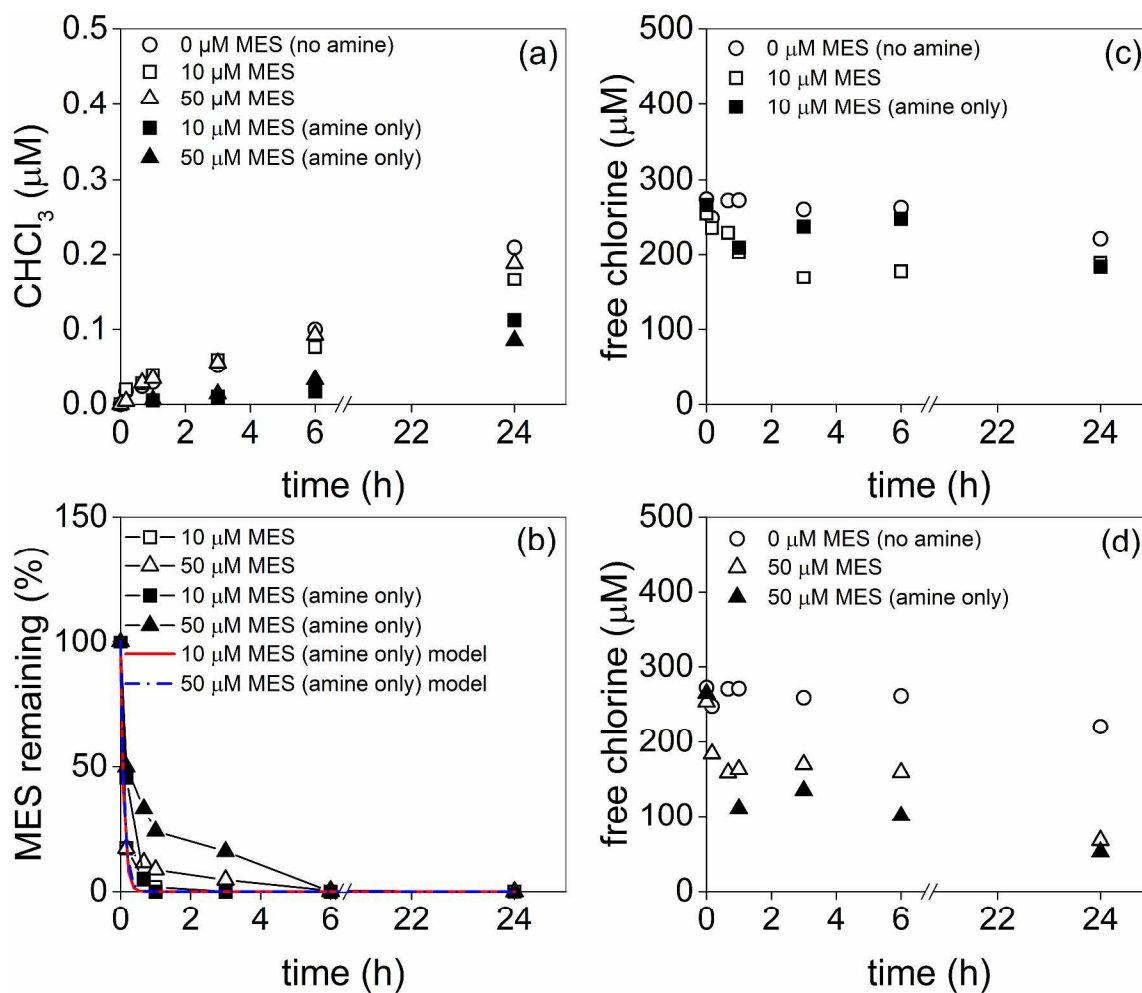
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163 **Figure S11.** Effect of MES on CHBr<sub>3</sub> formation when SA is exposed to varying HOBr doses (10  
164 – 100 μM) after 24 h ([MES]<sub>0</sub> = 10 μM; [SA]<sub>0</sub> = 10 μM; pH 7.1-7.2).

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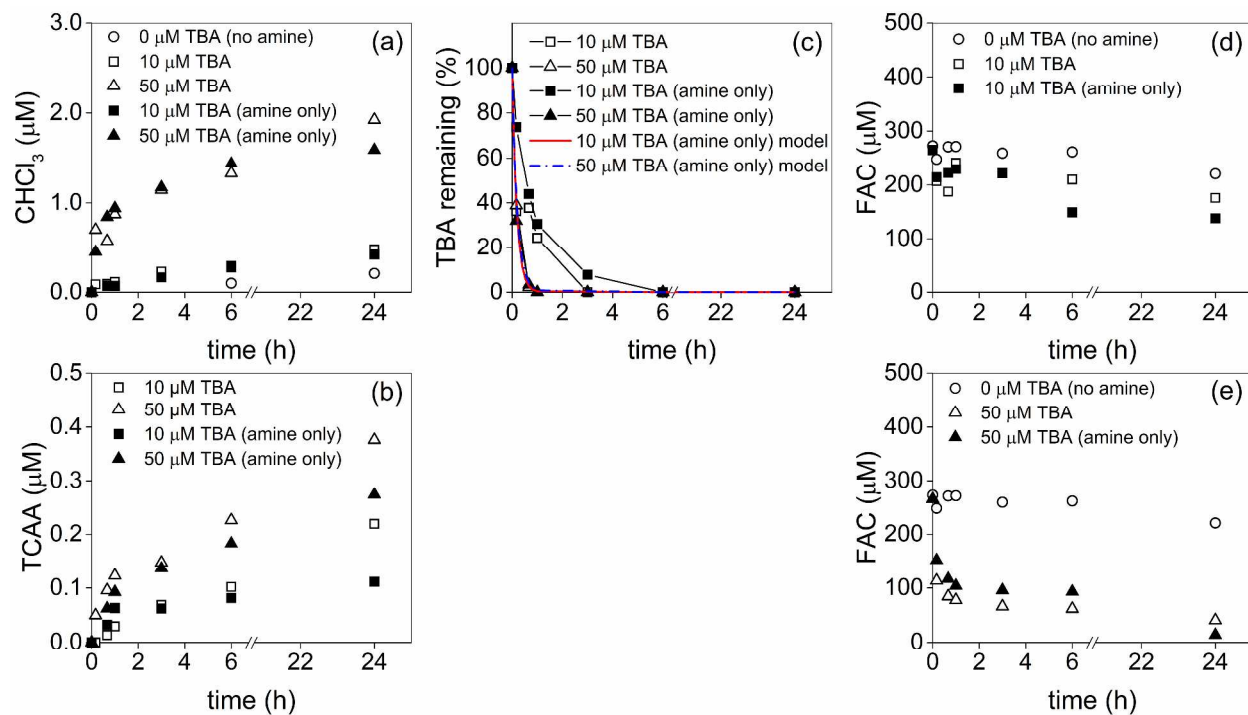


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169 **Figure S12.** Effect of MES on (a) CHCl<sub>3</sub> formation (b) MES % remaining and (c, d) residual  
 170 free chlorine when SRFA is chlorinated over 24 h ([SRFA]<sub>0</sub> = 10 μM (0.12 mg/L as C); [MES]<sub>0</sub>  
 171 = 0, 10 and 50 μM; [free chlorine]<sub>0</sub> = 280 μM (19.9 mg/L-Cl<sub>2</sub>); pH 7.1-7.2).

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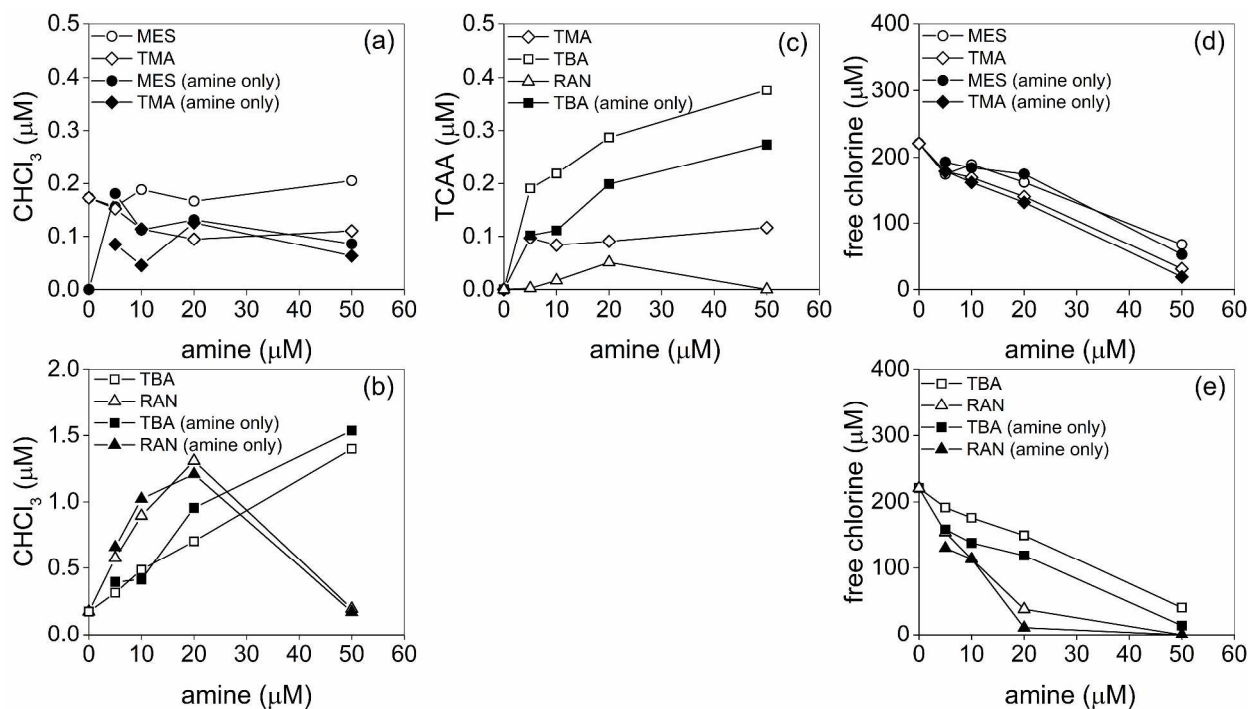


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175 **Figure S13.** Effect of TBA on (a)  $\text{CHCl}_3$  formation (b) TCAA formation (c) TBA % remaining  
 176 and (d, e) residual free chlorine when SRFA is chlorinated over 24 h ( $[\text{SRFA}]_0 = 10 \mu\text{M}$  (0.12  
 177 mg/L as C);  $[\text{TBA}]_0 = 0, 10$  and  $50 \mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$  (19.9 mg/L- $\text{Cl}_2$ ); pH 7.1-7.2).

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181 **Figure S14.** Effect of varying MES, TMA, TBA and RAN doses (0 - 50  $\mu\text{M}$ ) on (a, b)  $\text{CHCl}_3$  (c)  
 182 TCAA formation and (d, e) residual free chlorine when SRFA is chlorinated for 24 h ( $[\text{SRFA}]_0 =$   
 183  $10 \mu\text{M}$ ;  $[\text{free chlorine}]_0 = 280 \mu\text{M}$  ( $19.9 \text{ mg/L-C}_2$ ); pH 7.1-7.2).

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